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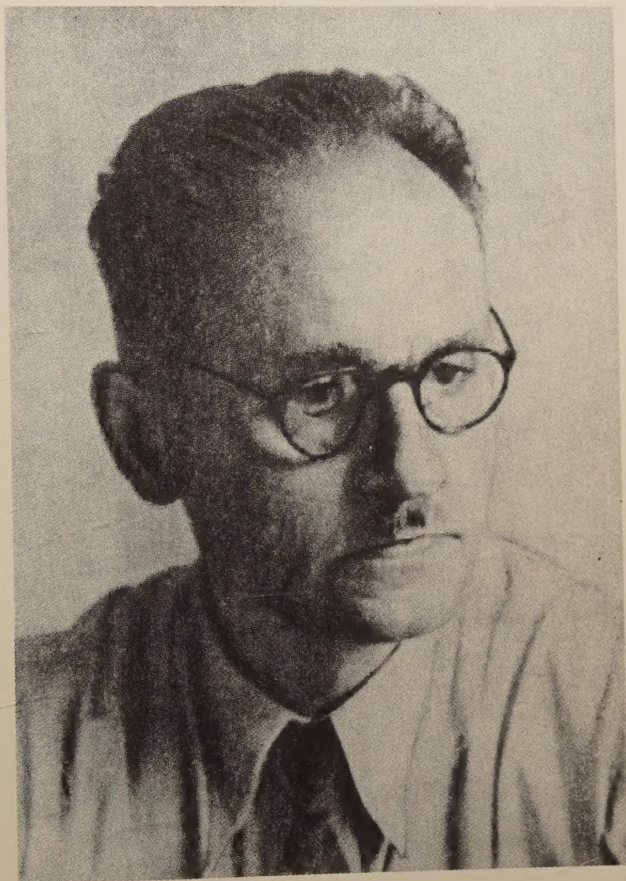
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ANDRZEJ SOŁTAN (1897—1959)





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The 10th of December 1959 Polish physics suffered a tremendous loss by the sudden death of Professor Andrzej (Andrew) Sołtan, a leading Polish nuclear physicist. This quite unexpected passing away of Professor A. Sołtan occurred just in the period when Polish physics, especially the nuclear physics in this country, urgently needed his care and guidance.

Everybody who knew or only approached Professor Sołtan was not only under the influence of his noble and attractive personality, but also full of admiration for the clarity and vividness of his mind, for the amplitude and depth of his knowledge in all, even very remote, branches of physics and for his excellent experimental talents.

Andrzej Sołtan was born in Warsaw the 25th of November 1897. He completed his secondary education in Petrograd (Russia) during World War I. After his return to Poland he began to study physics at the Warsaw University. Very early, even before being graduated, Andrzej Sołtan became assistant at the Institute of Experimental Physics of the Warsaw University and worked in close collaboration with Professor Stefan Pieńkowski who just initiated the organization of his well-known research school in molecular physics. Simultaneously with his numerous didactic and administrative duties in the Institute, Andrzej Sołtan began under the leadership of Prof. Pieńkowski experimental research work on the band spectrum of mercury. In particular this work concerned the emission spectrum of mercury hydrate molecules under electrical discharges. The first results of his investigations Andrzej Sołtan reported in 1924 at the II General Meeting of the Polish Physical Society held in Cracow. In 1925 and 1926 two papers appeared in the "*Comptes Rendus des Séances de la Société Polonaise de Physique*" containing the results of these and subsequent works on the same subject. Presenting his doctor thesis on band spectra in mixtures of hydrogen and mercury vapour, Andrzej Sołtan obtained the Ph. D. degree in 1926. Shortly afterwards he published together with S. Szczeniowski in the same Proceedings of the Polish Physical Society a paper entitled "*Caractéristiques de sensibilité de quelques émulsions photographiques*".

The following year, due to the support of Prof. Pieńkowski, Dr Sołtan was granted a fellowship enabling him to spend a year in Paris on research work in X-ray spectroscopy at the laboratory of Maurice de Broglie. Together with Jean Thibaut they worked on the so called "intermediate domain" and succeeded to fill this empty

gap in the experimental spectrum of electromagnetic radiation between the farthest ultraviolet and the region of the softest then known X-rays. In these investigations they applied a method of ruled diffraction gratings and beams of X-rays incident at nearly glancing angles. Thus this disquieting gap in the electromagnetic spectrum has been experimentally closed. The conspicuous results of these investigations of Sołtan and Thibaut have been published in the "Comptes Rendus des Séances de l'Académie des Sciences de Paris" and in the "Journal de Physique et le Radium".

After his return to Warsaw Dr Sołtan is again very active, mainly in organization and administrative work, and in enlarging and modernizing the Institute of Experimental Physics of the Warsaw University. In this work he became again the main collaborator of Prof. Pieńkowski. Due to these extensive efforts the Institute was transformed into one of the best organized and equipped physical laboratories in Europe. In spite of his extremely absorbing occupations Dr Sołtan still had some time for experimental research work. The results of this work were published in two papers which appeared in the "C. R. Soc. Polon. Phys." and in the "Acta Physica Polonica". The first of these papers contains the description of a new model of a capillary mercury lamp constructed by Dr Sołtan. This type of mercury lamp proved to be very convenient in different optical investigations and is still widely used in many spectroscopical laboratories. In the second paper Dr Sołtan reports the results of his newly commenced experiments carried on with unusual tenacity and aiming at discovering the influence of chemical bonds on the absorption coefficients of X-rays.

In 1933 Dr Sołtan received a fellowship of the Rockefeller Foundation enabling him to spend a year on research work in the Kellogg Laboratory, California Institute of Technology, Pasadena. There he started his new line of research work — nuclear physics, to which he remained faithful through the rest of his life. In this so dramatic and important period in the development of nuclear physics, soon after the first completely artificial transmutation of elements had been performed, and the neutron and the positive electron detected, Dr Sołtan entered a team doing experiments on nuclear reactions caused by artificially accelerated ions. In collaboration with C. C. Lauritsen and H. R. Crane results were obtained of fundamental importance for the further progress of nuclear physics. Crane, Lauritsen and Sołtan have proved the emission of neutrons by different targets of light elements bombarded by high speed deuterons, this being the first experiment on the production of neutrons by artificially accelerated particles. The results of these important researches were published in four papers, one in the "C. R. Acad. Sci. de Paris" and three in the "Physical Review".

Back in Warsaw, Dr Sołtan began immediately the difficult task of creating in the Warsaw Institute of Experimental Physics of the University experimental facilities enabling him to continue the research work started in Pasadena. In spite of the tremendous amount of administrative duties at the post of a chief assistant (adjunkt) at the quickly growing Institute, he succeeded to build, almost with one's own hand, a cascade ion accelerator of the Greinacher type up to energies of about 800 kV. Using



this accelerator as a source of fast neutrons, he performed various experiments on nuclear reactions produced by these neutrons. In these investigations Dr Sołtan was helped by Prof. Ludwik Wertenstein, director of the Radiological Laboratory of the Warsaw Scientific Society, and Dr Jan Cichocki, who at the end 1938 replaced Dr Sołtan at the post of chief assistant at the Institute of Physics of the Warsaw University. The results of these works were published in four papers in 1937, 1938, and 1939, one of them in common with L. Wertenstein and two in common with J. Cichocki.

In 1938 on the ground of the paper on radio-isotopes of bromine Dr A. Sołtan habilitated at the Warsaw University and was promoted to the rank of docent (assistant professor) of experimental physics at this university.

About a year before the outbreak of World War II, Dr Sołtan gave up his post of a chief assistant at the Institute of Experimental Physics, Warsaw University, and became director of the physical research laboratory in the Philips works in Warsaw. Continuing his research work in the Institute of Experimental Physics, Warsaw University, he started simultaneously in his new, reorganized and enlarged, technical laboratory to carry into effect a project of building a small cyclotron. Unfortunately the fulfilment of this ambitious enterprise was interrupted by the outbreak of World War II.

During the German occupation in Poland Dr Sołtan was intensively engaged in the secret teaching of physics in the Warsaw underground University. In 1944 with the whole Warsaw Philips Works Dr Sołtan was evacuated to Vienna, as well as his cyclotron, which has been afterwards completely destroyed during the air bombardment of Vienna.

When the Soviet troops entered Vienna, Dr Sołtan returned to Poland. Since Warsaw was at that time completely devastated, Dr Sołtan started his work of rebuilding higher education in Poland on the post of professor of physics and director of the Physical Laboratory in the Institute of Technology in Łódź. In a very short time he performed there the great and difficult task of organizing lectures and student classes in physics.

At the same time the rebuilding of the Warsaw University together with its Institute of Experimental Physics carried out under the most energetic leadership of Professor S. Pieńkowski has made surprisingly quick progress. A new chair of atomic physics has been created in the Warsaw University and Professor Sołtan has been invited to occupy it. Soon he moved to Warsaw retaining still for some years the directorship of the Physical Laboratory at the Łódź Institute of Technology.

In 1946 on the invitation of the U. S. Government Professor Sołtan together with Professor Pieńkowski represented Polish science at the atomic bomb tests at the Bikini atoll in the Pacific Ocean. During both his crossings of the American continent Professor Sołtan renewed his pre-war bonds with several American nuclear physicists; this was of no minor importance for his further work.

The greatest efforts of Professor Sołtan were directed towards the creation in the



Institute of Experimental Physics of the Warsaw University of contemporary research facilities in nuclear physics. The Institute was completely rebuilt and substantially enlarged, a special new large hall was built to house a big high voltage accelerator, by a special financial support of the Government Professor Sołtan was enabled to order in the known Swiss firm E. Haefely, Basel, a one million volt cascade generator with an accelerating tube. This generator was mounted in the Warsaw Institute in 1950. Then Professor Sołtan started a very intensive program of work consisting in preparing and providing additional apparatus required for research work and, what was certainly his most important job, in teaching and preparing a sufficient of young physicists to carry on the research work in nuclear physics. He was successful to prepare in Warsaw in the course of several years a group of capable and well trained young physicists on which the further development of the research work in nuclear physics could be based.

In 1950 Professor Sołtan was elected corresponding member of the Polish Academy of Science and Letters (Polska Akademia Umiejętności) in Cracow. In 1952, he became corresponding member of the newly created Polish Academy of Sciences in Warsaw.

In 1952 the Institute of Physics of the Polish Academy of Sciences began its activities and Professor Sołtan became the director of its department of nuclear physics (called "Laboratory of Radioactive Isotopes"), which was housed together with his Laboratory of Atomic Physics in the building of the Institute of Experimental Physics of the Warsaw University. The creation of the new laboratory gave Professor Sołtan more financial means and more scientific and auxiliary personnel to extend the possibilities of the experimental work in nuclear physics.

Much more advanced possibilities for research work in nuclear physics in Poland arose after the establishment in 1955 of the Institute of Nuclear Research. Prof. Sołtan's Laboratory of Radioactive Isotopes was transferred from the Institute of Physics of the Polish Academy of Sciences, to the newly founded Institute. Prof. Sołtan became the first Director General of the Institute of Nuclear Research. The organization of this multispecialized Institute left him only very little time to devote himself to nuclear physics. Nevertheless, he was very successful in organizing both in the building of the Institute of Experimental Physics at the University and later in the Centre of Nuclear Research in Świerk near Warsaw model laboratories for research work in nuclear physics of low and medium energies. At Świerk this work is mainly concentrated on nuclear neutron reactions, basing on the research reactor EWA, which started to operate in June 1958, and on nuclear spectroscopy. A  $d + t$  fast neutron generator is now being put into operation and a 10 MeV linear proton accelerator is approaching its completion.

About a year before his death Professor Sołtan resigned from the post of the Director General of the Institute of Nuclear Research in order to have more time for individual research work in nuclear physics. He retained the post of the Director of the Physics Division of the Institute, as well as that of the Director of the Centre



of Nuclear Research at Świerk. At the same time he still remained President of the Scientific Council of the Institute of Nuclear Research. Professor Sołtan always paid vivid attention to every work in physics done in the Institute and was personally leading many research works of his numerous pupils and collaborators. A most excellent and universal specialist in the techniques of experimental work in various branches of physics, he was always an unsurpassed and generally admired adviser to anybody looking for his help. E.g. his approval of any mechanical shop work, in which he was also an expert, was always regarded as a highest praise.

In the course of the last two years of his life his personal interest was mostly directed towards plasma phenomena and thermonuclear reactions. He led in the Institute a small but enthusiastic group of research workers who did not only make theoretical studies but performed already some small scale experiments, on these subjects.

Besides many other official duties Professor Sołtan was an active member of both the State Council for the Application of Nuclear Energy and of the Committee for the Peaceful Applications of the Atomic Energy of the Polish Academy of Sciences. In the period 1951—1952 he was also acting as President of the Polish Physical Society.

Professor Sołtan was a member of the Scientific Council of the Joint Institute of Nuclear Research at Dubna (USSR) from the moment of its establishment. In this capacity Professor Sołtan took an active part in all sessions of the Council, exerting a beneficial influence on the development and activity of this international Institute.

Professor Sołtan attended as an official member of the Polish Delegation both the 1st in 1955 and the 2nd in 1958 International Conferences for the Peaceful Application of the Atomic Energy at Geneva. He attended also the International Conference on Nuclear Reactions in Amsterdam in 1956, the Rehovoth Conference on Nuclear Structure in 1958 and several others.

The role which Professor Andrzej Sołtan played in the history of Polish science is of a very great importance. The premature and quite unexpected loss of this eminent, very active and hard working man, exhibiting excellent health up to the last moment of his life, created an emptiness in Polish physics which it will be impossible to fill for many many years.

*Henryk Niewodniczański*

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# ZUR LOKALISIERUNG DER ENERGIE IN DER ALLGEMEINEN RELATIVITÄTSTHEORIE

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(Eingegangen am 3. Juni 1959)

Aufbauend auf Ergebnissen von Möller wird untersucht, in welchem Maße ein Energiebegriff, der sich auf eine affine Tensordichte  $\tau_i^k$  mit  $\tau_{i,k}^k = 0$  stützt, eine Lokalisierung gestattet.

## 1.

Ist  $M$  die Mannigfaltigkeit der Raum-Zeit-Punkte und erfüllt der auf  $M$  gegebene metrische Tensor  $g_{ik}$  die Einsteinschen Gleichungen

$$R_{ik} - \frac{1}{2} g_{ik} R = -\kappa T_{ik}$$

so sollte der Begriff der Energie  $E$  nur von der metrischen Fundamentalform  $ds^2 = g_{ik} dx^i dx^k$  und von einer (möglichen) Gesamtheit voneinander unabhängiger Beobachter abhängen. Es sollte deshalb  $E$  ein Funktional nur von  $ds^2$  und einer raumartigen Punktmenge  $\Omega$  aus  $M$  sein:

$$E = E[ds^2, \Omega]. \quad (1)$$

Es ist dann  $E$  der Energieinhalt des in  $\Omega$  lokalisierten (Teiles des) physikalischen Systems.

Wir können zur Vereinfachung annehmen, daß  $\Omega$  ein Stück einer raumartigen (3-dimensionalen) Hyperfläche ist. Man wird dann erwarten, daß  $E$  das Integral über eine Energiedichte ist, das über  $\Omega$  erstreckt ist:

$$E = \int_{\Omega} h dV \quad (2)$$

Versteht man hierbei unter  $dV$  das durch die Beschränkung der Metrik  $ds^2$  auf  $\Omega$  auf dieser Hyperfläche definierte Volumenelement, so ist  $dV$  nur von  $ds^2$  und  $\Omega$  abhängig. (1) ist deshalb genau dann erfüllt, wenn  $h$  nur von  $ds^2$ , von  $\Omega$  und von den auf  $\Omega$  liegenden Weltpunkten  $P$  abhängt:

$$h = h[ds^2, \Omega, P], \quad P \in \Omega \quad (3)$$

## 2.

Sei  $\Omega$  eine Hyperfläche und  $P_0$  einer ihrer Punkte. Es gibt dann eine Umgebung  $U$  von  $P_0$  und eine dort erklärte Funktion  $f$  mit

$$P \in \Omega \cap U \leftrightarrow f(P) - f(P_0) = 0, \quad P \in U \quad (4a)$$

und

$$\sum \left| \frac{\partial f}{\partial x^i}(P) \right| \neq 0 \quad \text{für } P \in U. \quad (4b)$$

Genau dann ist bekanntlich  $\Omega$  raumartig in den eben betrachteten Punkten, wenn  $\text{grad } f$  ein zeitartiges Vektorfeld ist.

Wir können  $\Omega$  somit durch Funktionen der Eigenschaft (4) charakterisieren. Damit die Funktionen  $f$  und  $f'$  die gleiche Hyperfläche  $\Omega$  charakterisieren, ist notwendig und hinreichend, daß die Pfaffschen Formen  $df$  und  $df'$  gleichzeitig auf  $\Omega$  verschwinden. Sind  $x^1, x^2, x^3$  drei Funktionen, die  $f$  zu einem Koordinatensystem  $\{x^i\} = \{x^1, x^2, x^3, x^4\}$  mit  $x^4 = f$  ergänzen, so heißt das

$$df' = A df + B_1 dx^1 + B_2 dx^2 + B_3 dx^3, \quad B_k(P) = 0 \quad \text{für } P \in \Omega. \quad (5)$$

Charakterisieren wir nun  $\Omega$  (stückweise) durch ein Koordinatensystem  $\{x^i\}$  und die Bedingung  $x^4 - x^4(P_0) = 0$ . Wenigstens für genügend kleine Stücke von Hyperflächen können wir dann

$$h = h[ds^2, \{x^i\}, P], \quad x^4(P) - x^4(P_0) = 0 \quad (6)$$

setzen mit irgendeinem Punkt  $P_0 \in \Omega$ .

Wegen (3) muß dann gelten

$$h[ds^2, \{x^i\}, P] = h[ds^2, \{y^i\}, P] \quad (7a)$$

falls

$$\frac{\partial y^4}{\partial x^k}(P) = 0 \quad \text{für } k = 1, 2, 3 \quad \text{und} \quad x^4(P) - x^4(P_0) = 0 \quad (7b)$$

ist.

Die Bedingung (7) ist notwendig und hinreichend für die Darstellung der Energiedichte  $h$  in der Form (3) und somit auch für die Darstellung der Energie in der Form (1). Mit anderen Worten: (7) sind die notwendigen und hinreichenden Bedingungen für die Lokalisierbarkeit der Energie.

## 3.

Die in (7) zugelassenen Koordinatentransformationen enthalten unter anderen diejenigen der Form

$$y^4 = x^4, \quad y^k = A^k(x^1, x^2, x^3), \quad k = 1, 2, 3. \quad (8)$$



Gegenüber diesen ist die Möllersche Energiedichte [1], [2]  $h$  invariant. Möllers Energiedichte ist aber nicht invariant gegenüber allen in (7) zugelassenen Transformationen.

Ist z. B.  $\Omega$  durch  $x^4 = 0$  gegeben, so ist  $\Omega$  auch durch  $y^4 = 0$  gegeben, wenn  $x^4 = s \cdot y^4$  und  $s \neq 0$  auf  $\Omega$  ist. Wir können nun  $x^r$  und  $y^r$  ( $r = 1, 2, 3$ ) so wählen, daß sowohl für die Komponenten  $g_{ik}$  des metrischen Tensors bezüglich  $\{x^i\}$  als auch für seine Komponenten  $g_{ik}'$  bezüglich  $\{y^i\}$  die Relation  $g_{i4} = g_{i4}' = 0$  für  $i = 1, 2, 3$  gilt. Betrachten wir mit den so konstruierten Koordinatensystemen die nach (7) zulässige Transformation

$$y^k = A^k(x^1, x^2, x^3, x^4), \quad k = 1, 2, 3, \quad y^4 = s \cdot x^4. \quad (9)$$

Gl. (7b) ist erfüllt, weil  $x^4$  auf  $\Omega$  konstant ist.

Wegen  $g_{i4} = 0$  für  $i \neq 4$  gilt nach Möller [1], [2]

$$h = \frac{2}{\kappa} \Delta \sqrt{-g_{44}}. \quad (10)$$

Hierbei ist  $\Delta$  der Laplace-Beltrami-Operator, der zu der auf  $\Omega$  induzierten Metrik gehört.  $\Delta$  hängt also nur von  $ds^2$  und  $\Omega$  ab. Beim Koordinatenwechsel (9) wird aber

$$g_{44} \rightarrow s^{-2} g_{44} = g_{44}' \quad (9a)$$

für Punkte von  $\Omega$  und somit wird

$$h = \frac{2}{\kappa} \Delta \sqrt{-g_{44}} \rightarrow h' = \frac{2}{\kappa} \Delta s^{-1} \sqrt{-g_{44}}. \quad (9b)$$

Offensichtlich kann  $s$  so gewählt werden, daß  $h \neq h'$  ist. Also ist in Möllers Formalismus

$$h \neq h[ds^2, \Omega, P] \quad \text{bzw.} \quad E \neq E[ds^2; \Omega] \quad (11)$$

#### 4.

Betrachten wir nun (11) im Hinblick auf den Möllerschen Eindeutigkeitssatz [2]. Hiernach gibt es nur eine Größe  $\mathcal{T}_i^k$ , die erstens eine affine Tensordichte ist, zweitens die Gleichung  $\mathcal{T}_{k,i}^k = 0$  erfüllt und deren zugeordnete Energiedichte  $h$  (mindestens) unter der Gruppe (8) invariant ist. Diese durch obige Forderungen eindeutig bestimmte Energiedichte  $h$  ist nach [2] gerade durch (10) gegeben. Da die Forderung, daß  $\mathcal{T}_i^k$  eine affine Tensordichte ist, im Wesentlichen aus der Forderung nach Invarianz der Gl.  $\mathcal{T}_{i,k}^k = 0$  entspringt, erlaubt Formel (11) folgenden Schluß:

Es gibt keine affine Tensordichte, die nur von der Metrik abhängt und die es gestattet, die Energie als Funktional raumartiger Gebilde zu betrachten.

Die beiden Forderungen:  $\mathcal{T}_i^k$  ist affine Tensordichte und  $\mathcal{T}_{i,k}^k = 0$  sind also mit der Forderung nach strenger Lokalisierbarkeit der Energie nicht vereinbar.

Diese Schlußfolgerung als auch die des Abschnittes 6 gelten allerdings nur unter der Annahme, daß  $\mathcal{T}_i^k$  höchstens Abteilungen zweiter Ordnung von  $g_{ik}$  enthält. Es erscheint jedoch unwahrscheinlich, daß sich durch Einführung höherer Ableitungen die Situation grundlegend ändern könnte.

## 5.

Der eben erwähnte Möllersche Eindeigkeitssatz gestattet es abzuschätzen, bis zu welchem Grade eine Lokalisierung der Energie vorliegen kann, wenn eine affine Tensordichte mit  $\mathcal{T}_{i,k}^k = 0$  zugrunde gelegt wird. Zu diesem Zwecke betrachten wir die vorgegebene raumartige Hyperfläche  $\Omega$  als eingebettet in eine einparametrische Schar  $\Sigma(\lambda)$  von Hyperflächen. Wir können annehmen, daß  $\Sigma(\lambda)$  für Werte von  $\lambda$  in der Nähe von  $\lambda = 0$  definiert ist und daß  $\Omega = \Sigma(0)$  ist. Eine solche Schar können wir beschreiben durch Gleichungen der Form  $f(P) = \lambda$  wobei  $\text{grad } f$  ein zeitartiges Vektorfeld ist. Insbesondere können wir  $f$  als vierte Komponente eines Koordinatensystems  $\{x^i\}$  gewählt denken:

$$P \in \Sigma(\lambda) \longleftrightarrow x^4(P) = \lambda.$$

Ist  $\{y^i\}$  ein anderes Koordinatensystem und soll  $y^4(P) = \lambda'$  dieselbe Schar von Hyperflächen (jedoch möglicherweise mit einem anderen Parameter) beschreiben, so muß die Gl. (7b) nunmehr für alle Punkte der Hyperflächenschar gelten. D. h. an Stelle von (7b) tritt die schärfere Forderung

$$\frac{\partial y^4}{\partial x^k} = 0 \quad \text{für } k = 1, 2, 3 \text{ und alle } P. \quad (13)$$

Es muß also sein:

$$y^4 = A(x^4); \quad y^k = A^k(x^1, x^2, x^3), \quad k = 1, 2, 3, \quad (14)$$

wobei wir noch  $g_{i4} = g'_{i4} = 0$  für  $i \neq 4$  vorausgesetzt haben.

Aus (14) folgt

$$g^{44} \rightarrow \left( \frac{\partial A}{\partial x^4} \right)^{-2} g_{44}.$$

Möllers  $h$  geht deshalb wegen (10) in

$$\frac{2}{\kappa} \Delta \left( \frac{\partial A}{\partial x^4} \right)^{-1} \sqrt{-g_{44}} = \left( \frac{\partial A}{\partial x^4} \right)^{-1} \cdot \frac{2}{\kappa} \Delta \sqrt{-g_{44}}$$

über, da  $\partial A / \partial x^4$  auf jeder Hyperfläche der Schar  $\Sigma(\lambda)$  konstant ist. Mit der Konstanten

$$\left( \frac{\partial A}{\partial x^4} \right)_{x^4=0} = a$$



transformiert sich also die Möllersche Energiedichte unter (14) gemäß

$$h \rightarrow a^{-1} h \quad (15a)$$

und somit

$$\int_{\Omega} h dV \rightarrow a^{-1} \int_{\Omega} h dV. \quad (15b)$$

Aus mathematischen Gründen erscheint es unwahrscheinlich, koordinatenunabhängige Bedingungen einzuführen, die bewirken, daß nur diejenigen Transformationen (14) mit  $\gamma^4 = x^4$  zulässig sind.

(15a) zeigt aber, daß wenigstens der Quotient  $h(P_2)/h(P_1)$  für zwei Punkte von  $\Omega$  koordinatenunabhängige Bedeutung besitzt. Dies kann man so aussprechen: Sei  $h$  Möllers Energiedichte, dann ist

$$\frac{h(P_1)}{h(P_2)} = \Phi [ds^2, \Omega, \Sigma(\lambda), P_1, P_2]$$

mit  $P_1, P_2 \in \Omega$  und  $\Omega = \Sigma(0)$  (16)

Hierbei ist  $\Sigma(\lambda)$  eine Schar raumartiger Hyperflächen, die  $\Omega$  enthält.

## 6.

Obwohl unwahrscheinlich, wollen wir doch annehmen, wir könnten eine zusätzliche Bedingung  $\alpha$  einführen, die die zugelassenen Koordinatentransformationen nicht nur auf (14) sondern sogar auf (8) beschränkt. Unter solchen günstigen Umständen hätten wir an Stelle von (16)

$$h(P) = \Phi' [ds^2, \Omega, \Sigma(\lambda), \alpha, P]$$

mit  $P \in \Omega, \quad \Omega = \Sigma(0)$  (17)

zu schreiben.

Wir bemerken, daß nach dem Vorhergehenden und nach Möllers Eindeutigkeitssatz durch (17) die maximale Möglichkeit für die Lokalisierbarkeit des Energiebegriffes unter den gemachten Voraussetzungen über  $\mathcal{T}_i^k$  gegeben ist. Jedoch ist (17) und noch prägnanter die daraus folgende Abhängigkeit

$$E = E [ds^2, \Omega, \Sigma(\lambda), \alpha], \quad \Omega = \Sigma(0) \quad (18)$$

sehr fragwürdig. Tatsächlich müßte in die Messung der Energie durch auf  $\Omega$  befindliche Beobachter die „Geschichte der Beobachter“ (und nicht die des Systems!) eingehen. D. h. die Energie würde nicht nur vom Bewegungszustand der Beobachter bei der Messung abhängen. Dies ist aber im Rahmen der klassischen Physik schwerverständlich. Will man also diese Härten der Interpretation

umgehen, dann muß die Voraussetzung, daß  $\mathcal{T}_i^k$  eine affine Tensordichte mit  $\mathcal{T}_{i,k}^k = 0$  ist, fallengelassen werden. Eine kleine Chance besteht vielleicht auch in der Einführung höherer Ableitungen.

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# WAVE EQUATIONS INVARIANT UNDER DISCONTINUOUS GROUPS AND THE PROBLEM OF NUCLEAR FORCES

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It is shown that physical space has only the role of a representation-space of a certain group. In a consequently discontinuous theory, space-time, therefore, may be left topological but the fundamental group is to be taken discontinuous. A 2-dimensional theory of nuclear forces invariant only under a discontinuous rotation group is developed. Hence an angular periodicity of the nuclear forces results. 3 and 4-dimensional generalizations lead to the non-euclidianity of space and space-time and thus may serve as physical supports to Einstein's gravitation theory. It is shown that theories invariant under discontinuous groups don't contain conservation laws.

## § 1. About the deduction of wave equations from groupal invariance conditions

The wave equations of quantum physics are completely determined by groupal invariance conditions. Thus e. g. the Klein-Gordon eq. is the most general homogeneous, linear partial differential eq. of second order with constant coefficients<sup>1</sup> invariant under the Lorentz group (L. G.). Yet, all considered groups (in the case above mentioned the L. G.) are continuous. But in the case of a consequent quantum-theory such topological (continuity) pretensions are not justified, as they contradict the fundamental conception of quantum physics according to which the structure of universe is discontinuous. Though concerning atomic phenomena the topological approximation concords with experiment, its extrapolation to nuclear phenomena where discontinuous structure could be observed is not at all justified. W. Heisenberg (1936, 1938, 1939, 1939) tried to give an account of discontinuous universe structure, by introducing an elementary length  $l \sim 10^{-13}$  cm. Yet a lattice model of universe with the periodicity constant  $l$  rises paradoxes (Schild 1948). In order to analyse whether such a method is indicated or not we shall reason as follows. In the wave eqs. there appear the spacial and temporal coordinates  $x_i$ ,  $ct$ . On one hand we should interpret them as notations for the physical quantities: space, time. On the other

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<sup>1</sup> Such eqs. we shall call in the following simply: linear while in the case of variable coefficients we shall speak of semilinear eqs.



hand they appear as coordinates in a representation-space of a linear representation of the group under which the wave eq. is invariant.

At the construction of the formalism attached to the respective wave eq. latter interpretation is necessary and sufficient. Insisting yet upon a unification of the two interpretations we are led to the idea that *physical space-time is but a representation space of a group*. In order to make clear what is to be understood by this, let us consider an example. In the transformation

$$\begin{aligned}x' &= x \cos \varphi - y \sin \varphi \\y' &= x \sin \varphi + y \cos \varphi\end{aligned}\tag{1.1}$$

$x, y$  have no more meaning than that to be the components of a vector in a space in which there is defined a representation of the group of plane rotations (P. R. G.) Concerning the representation (1.1) it should be observed that this representation is irreducible in the field of real numbers as there doesn't exist any real one-dimensional subspace of the plane invariant under P. R. G. Thus if  $x, y$  appear in a differential eq. to be constructed of invariance conditions under (1.1) it is sufficient to remain at this interpretation for  $x, y$ .

If the group is continuous its representation-space will be topological too. But a representation-space of a group is representation-space of any of its subgroups (under the induced representation). Thus the same *topological* space may be the representation-space also of a discontinuous subgroup of the initial continuous group. Thus *it is not necessary to pass to a discontinuous physical space* not even in a consequently discontinuous theory (i. e. a theory invariant under a discontinuous group) as the role of physical space is limited to that of a representation-space of the group which, as we have just seen, may be topological even for a discontinuous group.

Thus a consequently discontinuous theory can start from a differential eq. (and not e. g. from an eq. with finite differences) as this means to claim the continuity of  $x, y, z$  i. e. the continuity of the representation-space which is, without any physical restrictions as we have seen, admissible. Concerning the discontinuous group, we shall choose it as a subgroup of the continuous group of the approximative theory and the quantization of the group will lead us to a universal constant (not necessary with physical dimensions e. g. an angle). The discontinuous group evidently is not allowed to possess infinitesimal transformations.

A theory covariant under a discontinuous group will be called in the following *Q-covariant* under that group. E. g. a theory covariant under the discontinuous L. G. (discontinuous P. R. G.) will be called Q. L. covariant (Q. P. R. — covariant).

## § 2. Q-covariant formulation of the mesonic theory of nuclear forces

As it is well known the scalar mesonic theory of Yukawa is L. G.-covariant. The consideration of a static (time independent) problem in this theory must therefore start from an eq. invariant under the static subgroup of the L. G. i. e. the space rota-

tion group (S. R. G.) Such an equation was proposed by H. Yukawa:

$$\Delta_3 G - \mu^2 G = -g \delta(r) \quad (2.1)$$

where:

$$\Delta_3 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

$$r = \sqrt{x^2 + y^2 + z^2} \quad (2.2)$$

From this eq the well known potential with short ray of action of Yukawa:

$$G = \frac{g}{4\pi} \frac{e^{-\mu r}}{r} \quad (2.3)$$

is obtained.

For not complicating too much our further considerations we shall limit them to the equivalent plane problem i. e. the problem invariant under P. R. G. when instead of eq. (2.1) we have:

$$\Delta_2 G - \mu^2 G = -g \delta(r) \quad (2.4)$$

where:

$$\Delta_2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}$$

$$r = \sqrt{x^2 + y^2} \quad (2.5)$$

Also in this case a potential with short ray of action is obtained.

$$G = \frac{g}{2\pi} k_0(|\mu| r) \quad (2.6)$$

(for the proof see Appendix I).

Before passing to the Q. P. R.-invariant eq. let us observe that also the eq.<sup>2</sup>

$$\Delta_3 G - \frac{l^{-1}}{r} G = -g \delta(r) \quad (2.7)$$

invariant under the continuous S. R. G., leads to potentials with short ray of action.

In fact the singular solution of this eq. is (see Appendix II):

$$G(r) = g \frac{l^{-1}}{2\pi} \sum_{n=1}^{\infty} e^{-r \frac{l^{-1}}{n}} \frac{(n-1)!}{n} \times$$

$$\times \sum_{k=0}^{n-1} (-1)^{k+1} \frac{\left(r \frac{l^{-1}}{n}\right)^k}{(n-k-1)! (k+1)! k!} \quad (2.8)$$

Eq. (2.7) differs of eq. (2.1) by being semilinear while (2.1) is linear.

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<sup>2</sup>  $l$  being a fundamental length of the theory (like the Compton wavelength  $\mu^{-1}$  in (2.1))

Looking for the Q. P. R.-invariant eq. we start from the plane equivalent of eq. (2.7):

$$\Delta_2 G - \frac{l^{-1}}{r} G = -g \delta(r) \quad (2.9)$$

which as (2.7), also admits solutions with short ray of action.

We shall quantize the P. R. G. as given by (1.1) to:

$$\begin{aligned} x' &= x \cos n\varphi_0 - y \sin n\varphi_0 \\ y' &= x \sin n\varphi_0 + y \cos n\varphi_0 \\ \varphi_0 &= 2\pi/\nu \\ \nu &= \text{universal constant} \end{aligned} \quad (2.10)$$

where  $x, y$  are coordinates in the same topological representation-space as  $x, y$  were in (1.1). This is admissible as we have seen in § 1.

For passing to a Q. P. R.-invariant eq. it is sufficient that for the coefficient of  $G$  in the first member of eq. (2.9) instead of  $-l^{-1}/r$ , which is a P. R. G.-invariant function, there should be chosen a function which should be Q. P. R. invariant without being also invariant under the continuous P. R. G. (evidently any function invariant under the continuous P. R. G. is also Q. P. R.-invariant, but not also conversely so that such a choice is possible). In order to choose this function we shall reason as follows. The function  $-l^{-1}/r$  is up to the constant  $-l^{-1}$  equal to the reciprocal of the function  $z = r = \sqrt{x^2 + y^2}$  representing in the space  $x, y, z$  a cone, the generatrix of which makes an angle of  $45^\circ$  with the plane  $xOy$  (fig. 1). This surface is evidently invariant under the P. R. G. of the  $xOy$  plane. A surface Q. P. R.-invariant, yet not also invariant under the continuous P. R. G. of the  $xOy$  plane is the regular  $\nu$ -faced pyramid<sup>3</sup> inscribed in the cone of Fig. 1,  $\nu$  being the constant of (2.10). The eq. of this pyramid is:

$$\begin{aligned} z = & \frac{\sin(m+1)\frac{2\pi}{\nu} - \sin m\frac{2\pi}{\nu}}{\sin \frac{2\pi}{\nu}} x + \\ & + \frac{\cos m\frac{2\pi}{\nu} - \cos(m+1)\frac{2\pi}{\nu}}{\sin \frac{2\pi}{\nu}} y \end{aligned} \quad (2.11)$$

$$(m = 0, 1, 2, \dots, \nu - 1)$$

<sup>3</sup> It should be remarked that this pyramid is invariant also under a lot of symetries with respect to planes passing through the axis of the pyramid. These superflue symetries could be eliminated choosing instead of the pyramid a surface like that in fig. 2.



Now the Q. P. R.-invariant eq. will be:

$$\Delta_2 G - \frac{l^{-1}}{z} G = -g \delta(r) \quad (2.12)$$

with  $z$  given by (2.11).

Evidently the singular solution of this eq. is a periodical function of  $\varphi$  with the period  $\varphi_0$  (of course it also possesses a short ray of action). Thus the potential of

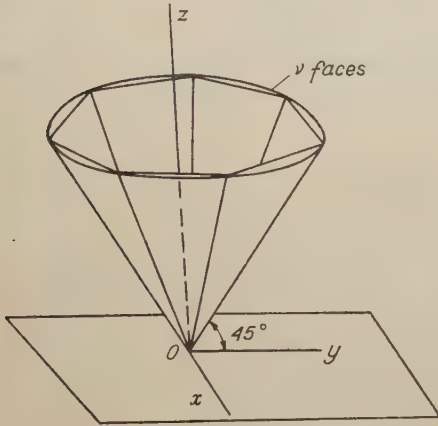


Fig. 1

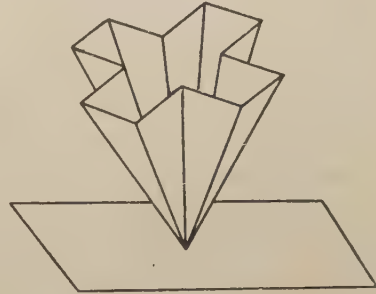


Fig. 2

nuclear forces and thus *nuclear forces themselves are periodical functions of  $\varphi$* . This fact could be verified experimentally; a determination of the constant  $\nu$  could be realised. Of course  $\varphi_0$  is very small and consequently  $\nu$  very large.

### 3. Observations

1. The angle  $\varphi_0$  is neglectible with atomic phenomena, nevertheless it ought to be observed with nuclear phenomena.

2. Our method of deduction of the eqs. (2.9), (2.12) includes a rather arbitrary step by the choice of the function  $z$  (2.11). Yet the arbitrariness of this step is not greater than that is done when linearity is claimed from eq. (2.1). A better choice of the function  $z$  must start of experimental data.

3. We treated a simplified 2-dimensional model. Really we ought to have started from a 3-dimensional corresponding to the S. R. G. (eq. 2.7). In this case as Q. S. R. G. would have appeared the group of a regular polyhedron. But it is well known that there exist but 5 groups because of the fact that the sum of the angles of a triangle must be  $180^\circ$ . These five polyhedra correspond to very high values of  $\varphi_0$  what is inadmissible. Yet this is not an impediment to the generalisation of our method because of the following. Regular polyhedra with an arbitrary high number of faces can be constructed in a non-euclidean space where the sum of the angles of a triangle is

high enough (of course  $> 180^\circ$  i. e. an elliptical space). This effect seems to be very likely, as by this Einstein's gravitation theory could be interpreted as the theory of global curvature of space due to the statistical behaviour of many individual curvatures due to Q-covariance of nuclear phenomena. Of course generalization to 4-dimensional space-time and other transformation properties of the wave function (e. g. spinorial) comport but mathematical difficulties.

4. As conservation laws in theories covariant under continuous groups are due to this covariance by means of the Noether-theorem, where the existence of infinitesimal transformations is essential, in a Q-covariant theory conservation laws are excluded. This means that in nuclear phenomena conservation laws are not anymore valuable. Such a result would also offer a physical justification to Hoyle's (1948, 1949) macroscopical conceptions.

5. It should be observed that the intrinsic structure of physical space is not essential in the theory, its significance being limited to that of a representation space. Thus in physics not space is fundamental, but the group i. e. the wave equations, i. e. the particles. This idea is related to some of the philosophical ideas recently expressed by W. Heisenberg (1958).

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### Appendix I.

#### *Proof of relation (2.6)*

The singular solution of eq. (2.4) is:<sup>1</sup>

$$G(x) = \frac{g}{4\pi^2} \int \frac{e^{i\vec{k}\vec{r}}}{k^2 + \mu^2} d^2 k \quad (I.1)$$

Choosing the unity vector  $\vec{k}_1$  in the direction of  $\vec{r}$ :

$$\vec{k}\vec{r} = kr \cos \varphi \quad (I.2)$$

and

$$d^2 k = dk_1 dk_2 = k dk d\varphi \quad (I.3)$$

By (I.1), (I.2), (I.3) we obtain:

$$G(r) = \frac{g}{4\pi} \int_0^\infty \frac{k dk}{k^2 + \mu^2} \int_0^{2\pi} e^{ikr \cos \varphi} d\varphi \quad (I.4)$$

But (see Watson (1945) § 2.2: (5)):

$$\int_0^{2\pi} e^{ikr \cos \varphi} d\varphi = 2\pi J_0(kr) \quad (I.5)$$

<sup>1</sup> The solution of the homogeneous eq. is put as usually equal zero.

By (I.4), (I.5) we have:

$$G(r) = \frac{g}{2\pi} \int_0^{\infty} \frac{k J_0(kr)}{k^2 + \mu^2} dk \quad (\text{I.6})$$

There exists the relation (see Watson (1945) § 13.6: (2))

$$\int_0^{\infty} \frac{k^{\nu+1} J_{\nu}(kr)}{(k^2 + \mu^2)^{\lambda+1}} dk = \frac{r^{\lambda} \mu^{\nu-\lambda}}{2^{\lambda} \Gamma(\lambda+1)} K_{\nu-\lambda}(|\mu| r) \quad (\text{I.7})$$

Putting  $\nu = \lambda = 0$  into (I.7):

$$\int_0^{\infty} \frac{k J_0(kr)}{k^2 + \mu^2} dk = k_0(|\mu| r) \quad (\text{I.8})$$

By (I.6) and (I.8) finally:

$$G(r) = \frac{g}{2\pi} k_0(|\mu| r) \quad (\text{I.9})$$

(I.9) is just (2.6).

## Appendix II.

### *Proof of relation (2.8).*

In order to find the singular solution of eq. (2.7) (the solution of the homogeneous eq. is put as usually = 0) we shall appeal to the following method usual with semilinear eqs. Let be  $D$  a semilinear, homogeneous differential operator and let us consider the eq.:

$$DG = -\delta\delta(r) \quad (\text{II.1})$$

Be  $g_n$  the eigenfunctions of the eq.:

$$Dg_n = \gamma_n g_n \quad (\text{II.2})$$

corresponding to the eigenvalues  $\gamma_n$ . If the  $g_n$  form a complete orthonormalized system then

$$\delta(r) = \sum_n a_n g_n \quad (\text{II.3})$$

where:

$$a = g_n^*(0)$$

where the asterisk indicates complex conjugation.



By (II.1) and (II.3) we obtain:

$$G(r) = -d D^{-1} \delta(r) = -g D^{-1} \left( \sum_n a_n g_n \right) \quad (\text{II.5})$$

Considering (II.2), we can write (II.5):

$$G(r) = -g D^{-1} \sum_n a_n \frac{D g_n}{\gamma_n} = -g \sum_n a_n \frac{D^{-1} D g_n}{\gamma_n}$$

Finally:

$$G(r) = -g \sum_n a_n \frac{g_n}{\gamma_n} \quad (\text{II.6})$$

In the case of eq. (2.7):

$$D = \Delta_3 - \frac{l^{-1}}{r} \quad (\text{II.7})$$

In this case (see Sommerfeld (1951) ch. II, §1: (17), (4a), (2a)):

$$\begin{aligned} (a) \quad g_n(r) &= N \varrho^2 L_{n+2}^{2l+1}(\varrho) e^{-\frac{\varrho}{2}} P_l^m(\cos \vartheta) e^{im\varphi} \\ (b) \quad |m| &\leq l \\ (c) \quad \varrho &= 2r\sqrt{\gamma_n} \end{aligned} \quad (\text{II.8})$$

Symmetry condition with respect to  $\vartheta$  and  $\varphi$  leads to:

$$m = l = 0 \quad (\text{II.9})$$

Considering (II.8), (II.9) and the fact that (see Sommerfeld (1951) ch. I, §3: (12) and fig. 1) one obtains:

$$g_n(\varrho) = N_n L_n^1(\varrho) e^{-\varrho/2} \quad (\text{II.10})$$

The orthonormalization condition for  $m = l = 0$  is (see Sommerfeld (1951): ch. II §2: (16)):

$$N_n^2 = \left( \frac{l^{-3}}{n} \right)^3 \frac{(n-1)!}{2n (n!)^3} \frac{1}{4\pi}.$$

Hence

$$N_n = \frac{l^{3/2}}{\sqrt{8\pi}} \frac{n^{-5/2}}{n!} \quad (\text{II.11})$$

There is (see Sommerfeld (1951), ch. II § 2: (25), (25a), (20)):

$$L_n^1(\varrho) = \frac{d}{d\varrho} L_n(\varrho) = \frac{(n!)^2}{(n-1)! 1!} \left( \sum_{k=0}^{n-1} (-1)^k \frac{(n-1)!}{(n-k-1)! (k+1)! k!} \varrho^k \right)$$

as all terms of the sum for  $k \geq n$  vanish.

Thus:

$$L_n^1(\varrho) = (n!)^2 \sum_{k=0}^{n-1} (-1)^k \frac{\varrho^k}{(n-k-1)! (k+1)! k!} \quad (\text{II.12})$$

It should be mentioned that some authors write (II.12) with a supplementary factor  $-1$  (Schiff (1955) : (16.22)).

By (II.10), (II.11), (II.12) we have:

$$g_n(r) = \frac{l^{3/2}}{\sqrt{8\pi}} n^{-5/2} n! e^{-\varrho/2} \sum_{k=0}^{n-1} (-1)^k \frac{\varrho^k}{(n-k-1)! (k+1)! k!} \quad (\text{II.13})$$

Hence:

$$g_n^*(0) = g_n(0) = \frac{l^{3/2}}{\sqrt{8\pi}} n^{-3/2} \quad (\text{II.14})$$

(II.3), (II.4), (II.13), (II. 14). yields:

$$\delta(r) = \sum_{n=1}^{\infty} \frac{l^3}{8\pi} n^{-4} n! e^{-\varrho/2} \sum_{k=0}^{n-1} (-1)^k \frac{\varrho^k}{(n-k-1)! (k+1)! k!} \quad (\text{II.15})$$

But (see Sommerfeld (1951) ch. II 1 : (10))

$$\gamma_n = \left( \frac{l^{-1}}{2n} \right)^2 \quad (\text{II.16})$$

By (II.6), (II. 8c), (II.14), (II.16) we obtain finally:

$$\begin{aligned} G(r) &= g \frac{l^{-1}}{2\pi} \sum_{n=1}^{\infty} e^{-r \frac{l^{-1}}{n}/2} \frac{(n-1)!}{n} \times \\ &\times \sum_{k=0}^{n-1} (-1)^{k+1} \frac{\left( r \frac{l^{-1}}{n} \right)^k}{(n-k-1)! (k+1)! k!} \end{aligned} \quad (\text{II.17})$$

That is just (2.8) It's easy to see that the series in (II.17) converges for any value of  $r \neq 0$ . The exponential factor indicates the short ray of action of the potential.

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# A MOLECULAR THEORY OF LIGHT SCATTERING IN GASES AND LIQUIDS

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The general principles of a statistical-molecular theory of light scattering in an isotropic medium consisting of polar-anisotropic molecules are given.

A general, fundamental equation for the scattered intensity  $I$  is derived, containing the molecular factors  $F_{is}$  and  $F_{anis}$  which account for isotropic and anisotropic light scattering as brought about by the molecules of the medium. The molecular factors  $F_{is}$  and  $F_{anis}$  are discussed in detail for the case of gases and liquids possessing molecules whose linear dimensions are small with respect to the light wave-length. In such gases and liquids,  $F_{is}$  depends on the mean polarizability of the molecule and on the radial intermolecular correlations, whereas  $F_{anis}$  depends on the symmetry and anisotropy of polarizability of the molecules and on the orientational intermolecular correlations. From the fundamental equation giving the scattered intensity, general expressions for the optical anisotropy  $\Delta^2$  and degree of depolarisation  $D$  of the scattered light, and for Rayleigh's ratio  $S$  and the extinction coefficient  $h$  are derived. For ideal gases, these expressions reduce to the known formulas of Rayleigh-Born-Cabannes. For liquids the molecules of which exhibit the axial symmetry, the expressions obtained for  $D$ ,  $S$  and  $h$  differ from those of Cabannes-King-Rocard in the anisotropic term by the angular correlation factor  $R_{CM}$ , which also appears in the formulas for the Cotton-Mouton and Kerr constants. For compressed gases the molecular factors  $F_{is}$  and  $F_{anis}$  are expanded in inverse powers of the volume of the system. The coefficients of the expansion,  $A_S^{is}$ ,  $A_S^{anis}$  and  $B_S^{is}$ ,  $B_S^{anis}$ , termed, respectively, the first and second virial coefficients of isotropic and anisotropic light scattering, are computed for spherical molecules of variable polarizability and for axially symmetrical anisotropic molecules possessing a permanent dipole moment. Moreover, following Buckingham's method, the effect of the internal molecular field and the hyperpolarizability of the molecules on light scattering in liquids is accounted for. Finally, general relations between the quantities  $D$ ,  $S$  and  $h$  and formulas relating these quantities and the anisotropic term in Kerr's constant  $K_{anis}$  are derived. The relations thus obtained contain no molecular parameters and may serve for checking the theory by experimental results.

## 1. Introduction

The theory of classical scattering, in which the wave-length of the light is preserved, is due to Lord Rayleigh (1899), who considered a gas of spherical, non-absorbing molecules of linear dimensions small with respect to the wave-length.

Smoluchowski (1908) was the first to prove that light scattering in optically homogeneous media arises from the spontaneous, thermal fluctuations of their density. Einstein (1910), who developed Smoluchowski's ideas, proposed a "phenomenological"

i. e. thermodynamical theory of scattering in liquids whose molecules are spherical<sup>\*)</sup>. Gans (1923) generalized the Smoluchowski-Einstein theory for anisotropic molecules.

The „molecular” or electronic theory of the scattering of light in gases and liquids possessing optically anisotropic molecules is due to Born (1917, 1933), Cabannes (1921, 1929), King (1923), Rocard (1928) and others.

Investigations by the foregoing authors proved that light scattering by a medium consisting, quite generally, of anisotropic molecules is given by the superposition of the scattering on fluctuations of its density and of the scattering occurring on fluctuations of the optical anisotropy of the molecules. Moreover, Rocard (1928) proved that scattering, especially in the neighbourhood of the critical point, is affected by the fluctuations of the intermolecular field. The foregoing theories assumed molecular interaction between the molecules, spherical or anisotropic, to depend solely on their mutual distances. Clearly this was a weak point of these theories, since both in real gases and in liquids consisting of anisotropic or polar-anisotropic molecules the interaction between the latter is strongly dependent on their mutual orientation. Hence, in addition to radial correlations, a theory of light scattering by condensed media should also account for orientational intermolecular correlations.

Müller (1936) was the first to consider orientational-molecular interaction, using the method of Fowler-Debye, in his theory of scattering in non-polar liquids. Anselm (1947), Benoit and Stockmayer (1956), and Prins and Prins (1956) proposed theories of the degree of depolarisation of light scattered by real gases and liquids, wherein the orientational-molecular interaction is described by Zernike and Prins' (1927) correlation function, as generalized to account for orientation (cf. also Volkensteyn, 1951, and Weill, 1958). Buckingham and Stephen (1957) proposed a general theory of the degree of depolarisation of light scattered by a dense medium; their theory accounts i. a. for scattering on assemblies of spherical molecules and for the effect of hyperpolarizability of the polar molecules.

In a former paper (Kielich, 1958a), the author proposed a generalization of Born's „gas” theory (1933) to liquids; therein, in addition to light scattering on fluctuations of the density and of the anisotropy of polarizability of the molecules, account is taken of scattering arising from the orientational interaction of molecules of arbitrary symmetry. In the present paper a general, statistical-molecular theory of light scattering in an isotropic medium consisting of anisotropic-polar molecules of arbitrary symmetry is proposed.

## *2. Fundamental Statistical-Molecular Theory of Light Scattering in an Isotropic Medium*

We shall be considering an isotropic medium of volume  $V$  containing a large number  $N$  of identical, optically anisotropic, polar molecules. The origin  $O$  of the fixed system of reference ( $X_o$ ) is located at the centre of the volume. Let molecular

<sup>\*)</sup> A molecular theory of light scattering by optically isotropic molecules of a fluid is given by Fixman (1955).

systems of reference  $(x_i^{(p)})$ ,  $p = 1, 2, \dots, N$  be rigidly attached to each molecule of the medium. The position and orientation of the molecules in volume  $V$  are given by their configurational variables  $\tau = \tau(\mathbf{r}, \omega)$ ; here,  $\mathbf{r} = \{\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N\}$  are those determining the position, whereas  $\omega = \{\omega_1, \omega_2, \dots, \omega_N\}$  determine the orientation of the molecule.

The probability for a mutual configuration of the molecules in an element  $d\tau$  of the configurational space is

$$dP(\tau) = f(\tau) d\tau,$$

with  $f(\tau)$  being the configurational statistical distribution function. By classical statistical mechanics, we assume  $f(\tau)$  to be given by Gibbs' canonical distribution function

$$f(\tau) = C e^{-\frac{U(\tau)}{kT}}, \quad (2.1)$$

wherein  $C$  is the normalisation constant,  $k$  — Boltzmann's constant,  $T$  — the Kelvin temperature of the system and  $U(\tau)$  — its total potential energy.

*Electric field of scattered light.* Consider a parallel monochromatic light beam of electric field

$$\mathbf{E}(t) = \mathbf{E} e^{-i2\pi\nu t}$$

incident on the volume  $V$  of the medium.  $\mathbf{E}$  denotes the electric field amplitude,  $\nu$  — the frequency, and  $t$  — the time.

Thus, the electric field of the incident light beam at the centre of the  $p$ -th molecule of the medium situated at the distance  $\mathbf{r}_p$  from the origin  $O$  of the system  $(X_o)$  is of the form

$$\mathbf{E}(t)^{(p)} = \mathbf{E} e^{-i(2\pi\nu t - \mathbf{k} \cdot \mathbf{r}_p)}, \quad (2.2)$$

wherein

$$\mathbf{k} = \frac{2\pi}{\lambda} \mathbf{s}_0 = \frac{2\pi\nu}{c} \mathbf{s}_0,$$

with  $c$  and  $\lambda$  denoting the velocity and wave-length of the incident light, respectively;  $\mathbf{s}_0$  is the unit vector in the direction of propagation.

The electric field given by (2.2) induces the time dependent dipole moment

$$\mathbf{m}'(t)^{(p)} = \mathbf{m}'^{(p)} e^{-i(2\pi\nu t - \mathbf{k} \cdot \mathbf{r}_p)} \quad (2.3)$$

within the  $p$ -th molecule of the volume  $V$ . Here,  $\mathbf{m}'^{(p)}$  is the amplitude of the dipole moment of the  $p$ -th molecule. By classical electrodynamics, the dipole induced in the molecule radiates electromagnetic waves in all directions. In the present paper, only Rayleigh scattering, i. e. scattered light of the same wavelength  $\lambda$  as that of the incident light will be considered.

At considerable distances from the scattering system, the electric field of the light wave scattered by the  $p$ -th molecule of the medium is of the form (cf. Born, 1933)

$$\mathbf{E}'(t)^{(p)} = -\frac{4\pi^2}{\lambda^2 R_p^3} \{ \mathbf{R}_p \times [\mathbf{R}_p \times \mathbf{m}'^{(p)} e^{-i(2\pi\nu t - \mathbf{k} \cdot \mathbf{r}_p - \frac{2\pi}{\lambda} R_p)}] \}, \quad (2.4)$$



wherein  $\mathbf{R}_p = \mathbf{R}_0 - \mathbf{r}_p$  is the vector directed from the centre of the  $p$ -th molecule to the point at which the radiation is observed. The latter point is at the distance  $\mathbf{R}_0$  from the origin  $O$  of the system ( $X_o$ ). The distance at which the point of observation is situated is great with respect to the linear dimensions  $l$  of the scattering volume and with respect to  $r_p$ ; thus, the following expansion may be written:

$$R_p = |\mathbf{R}_0 - \mathbf{r}_p| = R_0 - \mathbf{s}' \cdot \mathbf{r}_p + |\mathbf{r}_p| \left\{ 0 \left( \frac{|\mathbf{r}_p|}{R_0} \right) + \dots \right\}, \quad (2.5)$$

wherein  $\mathbf{s}'$  is the unit vector in the direction of the observation vector  $\mathbf{R}_0 = \mathbf{s}' R_0$ , thus determining the direction of propagation of the scattered wave.

If  $R_0 \gg l \gg r_p$ , then  $R_p$  may be replaced by  $R_0$  everywhere in eq. (2.4) with the exception of the exponential factor, wherein, with respect to the expansion (2.5), the substitution is  $R_p = R_0 - \mathbf{s}' \cdot \mathbf{r}_p$ ; this yields

$$\mathbf{E}'(t)^{(p)} = -\frac{4\pi^2}{\lambda^2 R_0} e^{-i2\pi \left( \nu t - \frac{R_0}{\lambda} \right)} \{ \mathbf{s}' \times (\mathbf{s}' \times \mathbf{m}'^{(p)} e^{i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{r}_p}) \}, \quad (2.6)$$

with

$$\mathbf{k}' = \frac{2\pi}{\lambda} \mathbf{s}' = \frac{2\pi \nu}{c} \mathbf{s}'$$

denoting the wave vector of the scattered light.

By eq. (2.6), the total electric field resulting from the light wave scattered by all the molecules in volume  $V$  at the point of observation is given by

$$\mathbf{E}' \left( t + \frac{R_0}{c} \right) = -\frac{4\pi^2}{\lambda^2 R_0} \{ \mathbf{s}' \times (\mathbf{s}' \times \mathbf{M} e^{-i2\pi \nu t}) \}, \quad (2.7)$$

wherein

$$\mathbf{M} = \sum_{p=1}^N \mathbf{m}'^{(p)} e^{i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{r}_p} \quad (2.8)$$

denotes the amplitude of the total dipole moment induced in the medium of volume  $V$  by the electric field of the incident light wave of amplitude  $\mathbf{E}$ .

*Intensity of scattered light.* We shall now consider the total intensity of the light scattered by the volume  $V$ , in order to determine the component thereof transmitted by a Nicol prism analyzer at the point of observation. Let the direction of the vibration transmitted by the nicol be that determined by the unit vector  $\mathbf{n}$  perpendicular to the vector of observation  $\mathbf{R}_0 = R_0 \mathbf{s}'$ . Since now  $\mathbf{s}' \cdot \mathbf{n} = 0$ , the component of the electric field  $\mathbf{E}'$  in the direction of the unit vector  $\mathbf{n}$  is given by:

$$\mathbf{E}' \cdot \mathbf{n} = \frac{4\pi^2}{\lambda^2 R_0} \mathbf{M} \cdot \mathbf{n} e^{-i2\pi \nu t}. \quad (2.9)$$

The intensity of the light scattered by the volume  $V$  of an isotropic medium and transmitted by a nicol is defined as follows:

$$I_n \equiv \langle \mathbf{E}' \cdot \mathbf{n} (\mathbf{E}' \cdot \mathbf{n})^* \rangle_E; \quad (2.10)$$

herein, the symbol  $\langle \rangle_E$  stands for the statistical mean value in the presence of the electric field  $\mathbf{E}$  of the incident light beam, and the asterisk denotes a complex conjugate. Let  $\Phi = \Phi(\tau, \mathbf{E})$  denote an arbitrary state function of the system in the presence of the electric field  $\mathbf{E}$ ; then, with Gibbs' distribution (2.1), the statistical mean value of  $\Phi$  is determined at thermodynamical equilibrium of the system as follows:

$$\langle \Phi \rangle_E = C \int \int \dots \int \Phi(\tau, \mathbf{E}) e^{-\frac{U(\tau, \mathbf{E})}{kT}} d\tau_1 d\tau_2 \dots d\tau_N; \quad (2.11)$$

here,  $U(\tau, \mathbf{E})$  is the total potential energy of the system under consideration in the presence of the electric field  $\mathbf{E}$  of the incident light wave.

Substituting (2.9) in (2.10), the fundamental equation for  $I_n$  may be written as follows in tensor notation:

$$I_n = \frac{1}{R_0^2} \left( \frac{2\pi}{\lambda} \right)^4 \langle M_\sigma M_\tau n_\sigma n_\tau \rangle, \quad (2.12)$$

the summation indices  $\sigma, \tau$  assuming the values 1, 2, 3.

At not too great intensities of the incident light, the dipole moment  $\mathbf{M}$  induced within the volume  $V$  may be assumed to be a linear function of the electric field  $\mathbf{E}$ . The dipole moment may then be written as follows:

$$M_\sigma(\tau, \mathbf{E}) = A_{\sigma\tau} E_\tau = A_{\sigma\tau} e_\tau E, \quad (2.13)$$

wherein

$$A_{\sigma\tau} = \left( \frac{\partial M_\sigma}{\partial E_\tau} \right)_{E=0} \quad (2.14)$$

is the tensor of the optical polarizability of the medium of volume  $V$ , and  $\mathbf{e}$  is the unit vector in the direction of the electric field,  $\mathbf{E} = \mathbf{e} E$ .

By (2.13), eq. (2.12) yields for a spherical scattering sample of volume  $V$  in vacuum

$$I_n = \frac{I_0}{R_0^2} \left( \frac{2\pi}{\lambda} \right)^4 \left( \frac{n^2 + 2}{3} \right)^2 \langle A_{\sigma\tau} A_{\nu\varrho}^* n_\sigma e_\tau n_\nu e_\varrho \rangle, \quad (2.15)$$

wherein  $I_0 = \left( \frac{3}{n^2 + 2} \right)^2 EE^*$  is the incident light intensity within the spherical sample of refractive index  $n$ ; the symbol  $\langle \rangle$  without lower indice denotes the statistical mean value in the absence of an electric field ( $\mathbf{E} = 0$ ):

$$\langle \Phi \rangle = C \int \int \dots \int \Phi(\tau) e^{-\frac{U(\tau)}{kT}} d\tau_1 d\tau_2 \dots d\tau_N. \quad (2.16)$$

Since the unit vectors  $\mathbf{n}$  and  $\mathbf{e}$  satisfy the relations

$$e_\sigma n_\sigma = \cos \Omega_{en}, \quad e_\sigma e_\sigma = n_\sigma n_\sigma = 1,$$

averaging over all possible directions of  $\mathbf{n}$  and  $\mathbf{e}$  with respect to the fixed system of reference ( $X_o$ ) yields

$$\overline{n_o e_\tau n_\nu e_\rho} = \frac{1}{30} \{ (3 \cos^2 \Omega_{en} - 1) (\delta_{\sigma\tau} \delta_{\nu\rho} + \delta_{\sigma\rho} \delta_{\nu\tau}) + 2(2 - \cos^2 \Omega_{en}) \delta_{\sigma\nu} \delta_{\tau\rho} \}, \quad (2.17)$$

with  $\Omega_{en}$  denoting the angle subtended by the unit vectors  $\mathbf{e}$  and  $\mathbf{n}$ , and  $\delta_{\sigma\tau}$  being Kronecker's symbol:

$$\delta_{\sigma\tau} = \begin{cases} 1 & \text{for } \sigma = \tau \\ 0 & \text{for } \sigma \neq \tau \end{cases}.$$

The optical polarizability tensor  $A_{\sigma\tau}$  being Hermitian,  $A_{\sigma\tau} = A_{\tau\sigma}^*$ , and with respect to (2.17), eq. (2.15) yields the following general, fundamental equation for the intensity of the light scattered by an isotropic medium:

$$I_n = Q \{ 5 \cos^2 \Omega_{en} F_{is} + (3 + \cos^2 \Omega_{en}) F_{anis} \}, \quad (2.18)$$

wherein

$$F_{is} = \langle \delta_{\sigma\tau} \delta_{\nu\rho} A_{\sigma\tau} A_{\nu\rho}^* \rangle, \quad (2.19)$$

$$F_{anis} = \frac{1}{2} \langle (3\delta_{\sigma\nu} \delta_{\tau\rho} - \delta_{\sigma\tau} \delta_{\nu\rho}) A_{\sigma\tau} A_{\nu\rho}^* \rangle, \quad (2.20)$$

with

$$Q = \frac{I_0}{45R_0^2} \left( \frac{2\pi}{\lambda} \right)^4 \left( \frac{n^2 + 2}{3} \right)^2. \quad (2.21)$$

The quantities  $F_{is}$  and  $F_{anis}$  will be termed the molecular factors of *isotropic* and *anisotropic* light scattering, respectively. With (2.8) and (2.14),  $F_{is}$  and  $F_{anis}$  may be rewritten in general form involving molecular parameters

$$F_{is}(s) = \left\langle \delta_{\sigma\tau} \delta_{\nu\rho} \sum_{pq} \frac{\partial m_\sigma^{(p)}}{\partial E_\tau} \left( \frac{\partial m_\nu^{(q)}}{\partial E_\rho} \right)^* e^{-i\mathbf{s} \cdot \mathbf{r}_{pq}} \right\rangle, \quad (2.22)$$

$$F_{anis}(s) = \frac{1}{2} \left\langle (3\delta_{\sigma\nu} \delta_{\tau\rho} - \delta_{\sigma\tau} \delta_{\nu\rho}) \sum_{pq} \frac{\partial m_\sigma^{(p)}}{\partial E_\tau} \left( \frac{\partial m_\nu^{(q)}}{\partial E_\rho} \right)^* e^{-i\mathbf{s} \cdot \mathbf{r}_{pq}} \right\rangle, \quad (2.23)$$

wherein the quantity

$$\mathbf{s} \cdot \mathbf{r}_{pq} = (\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}_{pq} \quad (2.24)$$

determines the difference in phase between the light scattered by the  $p$ -th and  $q$ -th molecules of the medium, with  $\mathbf{r}_{pq} = \mathbf{r}_q - \mathbf{r}_p$  being the vector connecting their centres, and

$$\mathbf{s} = \mathbf{k} - \mathbf{k}' = \frac{2\pi}{\lambda} (\mathbf{s}_0 - \mathbf{s}'). \quad (2.25)$$

*The polarizability tensor of a molecule immersed in the medium.* As a first approximation, it may be assumed that within a moderately condensed medium the di-



pole moment is induced in the molecule only by the electric field  $\mathbf{E}$  of the incident light wave. If the medium is a condensed one, however, an internal field  $\mathbf{F}^{(p)}$  due to the charge distribution of all the other  $N-1$  molecules and superimposing its effect on that of the field  $\mathbf{E}^{(p)}$  appears and acts on the  $p$ -th molecule. The dipole moment induced in a molecule immersed within the condensed medium is given by (see Buckingham and Stephen 1957)

$$m_{\alpha}^{(p)} = \alpha_{\alpha\alpha}^{(p)} (E_{\alpha}^{(p)} + F_{\alpha}^{(p)}) + \frac{1}{2} \beta_{\alpha\alpha\beta}^{(p)} (E_{\alpha}^{(p)} + F_{\alpha}^{(p)}) (E_{\beta}^{(p)} + F_{\beta}^{(p)}) + \frac{1}{6} \gamma_{\alpha\alpha\beta\gamma}^{(p)} (E_{\alpha}^{(p)} + F_{\alpha}^{(p)}) (E_{\beta}^{(p)} + F_{\beta}^{(p)}) (E_{\gamma}^{(p)} + F_{\gamma}^{(p)}) + \dots \quad (2.26)$$

where  $\alpha_{\alpha\alpha}^{(p)}$  is the polarizability tensor, and  $\beta_{\alpha\alpha\beta}^{(p)}$ ,  $\gamma_{\alpha\alpha\beta\gamma}^{(p)}$  are the hyperpolarizability tensors describing the field dependence of the polarizability. These tensors are symmetric in all suffixes and have been discussed by Buckingham and Pople (1955 a).

The field  $F_{\alpha}^{(p)}$  may be computed by Kirkwood's method (1936). Namely, if the medium consists of anisotropic-polar molecules, and considering only dipolar interactions, we have

$$F_{\alpha}^{(p)} = - \sum_{q=1}^N T_{\alpha\beta}^{(pq)} (\mu_{\beta}^{(q)} + m_{\beta}^{(q)}), \quad (2.27)$$

wherein  $\mu_{\beta}^{(q)}$  is the permanent electric dipole moment of the isolated molecule, and the tensor of dipolar interactions is given as follows:

$$T_{\alpha\beta}^{pq} = \frac{1}{r_{pq}^3} (r_{pq}^2 \delta_{\alpha\beta} - 3 r_{pq\alpha} r_{pq\beta}); \quad (2.28)$$

the latter assumes non-zero values for  $p \neq q$  and is zero for  $p = q$ .

From eqs. (2.26) and (2.27), the following formula is obtained for the field  $F_{\alpha}^{(p)}$  at the centre of the  $p$ -th molecule of the medium:

$$\begin{aligned} F_{\alpha}^{(p)} = & F_{\alpha\alpha}^{(p)} - \sum_q T_{\alpha\beta}^{(pq)} \alpha_{\beta\gamma}^{(q)} E_{\gamma}^{(q)} + \sum_{qr} T_{\alpha\beta}^{(pq)} \alpha_{\beta\gamma}^{(q)} T_{\gamma\delta}^{(qr)} \alpha_{\delta\epsilon}^{(r)} E_{\epsilon}^{(r)} - \\ & - \sum_{qrst} T_{\alpha\beta}^{(pq)} \alpha_{\beta\gamma}^{(q)} T_{\gamma\delta}^{(qr)} \alpha_{\delta\epsilon}^{(r)} T_{\epsilon\eta}^{(rs)} \alpha_{\eta\lambda}^{(s)} E_{\lambda}^{(s)} + \\ & + \sum_{qrst} T_{\alpha\beta}^{(pq)} \alpha_{\beta\gamma}^{(q)} T_{\gamma\delta}^{(qr)} \alpha_{\delta\epsilon}^{(r)} T_{\epsilon\eta}^{(rs)} \alpha_{\eta\lambda}^{(s)} T_{\lambda\mu}^{(st)} \alpha_{\mu\theta}^{(t)} E_{\theta}^{(t)} - \dots \end{aligned} \quad (2.29)$$

with  $F_{\alpha\alpha}^{(p)}$  denoting the intermolecular field existing at the centre of the  $p$ -th molecule immersed in the medium when the electric field  $\mathbf{E}$  of the incident light wave is absent ( $\mathbf{E} = 0$ ). The field  $F_{\alpha\alpha}^{(p)}$  is given quite generally as follows:

$$F_{\alpha\alpha}^{(p)} = - \sum_{q=1}^N T_{\alpha\beta}^{(pq)} m_{\beta}^{(q)}, \quad (2.30)$$

wherein

$$m_{\beta}^{(q)} = \mu_{\beta}^{(q)} + \alpha_{\beta\gamma}^{(q)} F_{\gamma}^{(q)} + \dots \quad (2.31)$$

is the total dipole moment of the molecule immersed in the medium at  $\mathbf{E} = 0$ , or explicitly:

$$F_{\alpha\alpha}^{(p)} = - \sum_q T_{\alpha\beta}^{(pq)} \mu_{\beta}^{(q)} + \sum_{qr} T_{\alpha\beta}^{(pq)} \alpha_{\beta\gamma}^{(q)} T_{\gamma\delta}^{(qr)} \mu_{\delta}^{(r)} - \\ - \sum_{qrs} T_{\alpha\beta}^{(pq)} \alpha_{\beta\gamma}^{(q)} T_{\gamma\delta}^{(qr)} \alpha_{\delta\epsilon}^{(r)} T_{\epsilon\eta}^{(rs)} \mu_{\eta}^{(s)} + \dots \quad (2.23)$$

By (2.26), the polarizability tensor of the  $p$ -th molecule immersed in the condensed medium is given as follows:

$$\left( \frac{\partial m_{\sigma}^{(p)}}{\partial E_{\chi}^{(p)}} \right)_{E=0} = \left\{ \alpha_{\sigma\alpha}^{(p)} + \beta_{\sigma\alpha\beta}^{(p)} F_{\alpha\beta}^{(p)} + \frac{1}{2} \gamma_{\sigma\alpha\beta\gamma}^{(p)} F_{\alpha\beta}^{(p)} F_{\gamma\delta}^{(p)} + \dots \right\} \delta_{\alpha\chi} + \frac{\partial F_{\alpha}^{(p)}}{\partial E_{\chi}^{(p)}} \Big|_{E=0}, \quad (2.33)$$

or, with respect to the expansion (2.29), explicitly:

$$\left( \frac{\partial m_{\sigma}^{(p)}}{\partial E_{\chi}^{(p)}} \right)_{E=0} = \alpha_{\sigma\chi}^{(p)} - \sum_q \alpha_{\sigma\alpha}^{(p)} T_{\alpha\beta}^{(pq)} \alpha_{\beta\chi}^{(q)} e^{i\mathbf{k} \cdot \mathbf{r}_{pq}} + \\ + \sum_{qr} \alpha_{\sigma\alpha}^{(p)} T_{\alpha\beta}^{(pq)} \alpha_{\beta\gamma}^{(q)} T_{\gamma\delta}^{(qr)} \alpha_{\delta\chi}^{(r)} e^{i\mathbf{k} \cdot \mathbf{r}_{pr}} - \sum_{qrs} \alpha_{\sigma\alpha}^{(p)} T_{\alpha\beta}^{(pq)} \alpha_{\beta\gamma}^{(q)} T_{\gamma\delta}^{(qr)} \alpha_{\delta\epsilon}^{(r)} T_{\epsilon\eta}^{(rs)} \alpha_{\eta\chi}^{(s)} e^{i\mathbf{k} \cdot \mathbf{r}_{ps}} + \\ + \sum_{qrst} \alpha_{\sigma\alpha}^{(p)} T_{\alpha\beta}^{(pq)} \alpha_{\beta\gamma}^{(q)} T_{\gamma\delta}^{(qr)} \alpha_{\delta\epsilon}^{(r)} T_{\epsilon\eta}^{(rs)} \alpha_{\eta\lambda}^{(s)} T_{\lambda\mu}^{(st)} \alpha_{\mu\chi}^{(t)} e^{i\mathbf{k} \cdot \mathbf{r}_{pt}} - \dots \quad (2.34)$$

The foregoing expansion shows the polarizability tensor of a molecule immersed in a condensed medium to be constant in the first approximation only; generally, however, this tensor is a function of the intermolecular field.

*Potential energy of molecular interaction within the medium.* From the definition of eq. (2.16), in order to compute effectively the molecular factors  $F_{is}(s)$  and  $F_{anis}(s)$  given by (2.22) and (2.23), respectively, the potential energy  $U(\tau)$  of the mutual interaction existing between the  $N$  molecules immersed in the medium of volume  $V$  should be known. The energy  $U(\tau)$  is dependent, in general, on the structure of the molecules and on the thermodynamical state of the medium, and, in principle, consists of two terms

$$U(\tau) = U^{(1)}(\mathbf{r}) + U^{(2)}(\mathbf{r}, \omega), \quad (2.35)$$

$U^{(1)}(\mathbf{r})$  denoting the potential energy inherent in *radial* interaction of the molecules only, and  $U^{(2)}(\mathbf{r}, \omega)$  denoting that due to *radial-orientational* interaction.

For  $U^{(1)}(\mathbf{r})$ , the Lennard-Jones potential (1924) is usually applied (cf. Pople, 1954), of the form

$$U^{(1)}(r) = 4\epsilon^* \left\{ \left( \frac{r_0}{r} \right)^{12} - \left( \frac{r_0}{r} \right)^6 \right\}, \quad (2.36)$$

wherein the first term represents the repulsive energies and the second — the attractive. The quantity  $\epsilon^*$  represents the negative value of the lowest potential energy,  $r$  is the intermolecular distance and  $r_0$  — the value of  $r$  at which the attractive and repulsive energies exactly balance.

It is customary to include in  $U^{(2)}(\mathbf{r}, \omega)$  the energy of the Keesom dipole-dipole interaction, as well as those of the Debye-Falkenhagen permanent dipole-induced dipole interaction, the London anisotropic-dispersive interaction and, finally, the multipole molecular interactions. For anisotropic-dipolar molecules, by (2.32), Barker's expression (1953) in tensor notation is obtained for  $U^{(2)}(\mathbf{r}, \omega)$ :

$$U^{(2)}(\mathbf{r}, \omega) = \frac{1}{2} \sum_{pq} \mu_{\alpha}^{(p)} T_{\alpha\beta}^{(pq)} \mu_{\beta}^{(q)} - \frac{1}{2} \sum_{pqr} \mu_{\alpha}^{(p)} T_{\alpha\beta}^{(pr)} \alpha_{\beta\gamma}^{(r)} T_{\gamma\delta}^{(rq)} \mu_{\delta}^{(q)} + \\ + \frac{1}{2} \sum_{pqrs} \mu_{\alpha}^{(p)} T_{\alpha\beta}^{(ps)} \alpha_{\beta\gamma}^{(s)} T_{\gamma\delta}^{(sr)} \alpha_{\delta\epsilon}^{(r)} T_{\epsilon\eta}^{(rq)} \mu_{\eta}^{(q)} - \dots; \quad (2.37)$$

herein, the consecutive terms determine interaction within assemblies of two ( $pq$ ), three ( $pqr$ ), four ( $pqrs$ ), ... of the  $N$  molecules present within the volume  $V$  of the medium.

The fundamental equation (2.18) containing the factors  $F_{is}(s)$  and  $F_{anis}(s)$  as determined by (2.22) and (2.23), together with the polarizability tensor of the molecule as given by (2.33) and the potential energy of molecular interaction (2.35) jointly determine the general form of the statistical-molecular theory of light scattering by an isotropic medium of an arbitrary nature.

### 3. Light Scattering in Gases and Liquids.

*Factors  $F_{is}$  and  $F_{anis}$  for molecules exhibiting constant polarizability.* If the medium is but a moderately condensed one, the effect of the intermolecular field on the polarizability tensor of the molecule may be neglected in the expansion of eq. (2.34), and the expressions (2.22) and (2.23) may be written in the first approximation as follows:

$$F_{is}(s) = \langle \delta_{\sigma\tau} \delta_{\nu\varrho} \sum_{pq} \alpha_{\sigma\tau}^{(p)} \alpha_{\nu\varrho}^{(q)*} e^{-i\mathbf{s} \cdot \mathbf{r}_{pq}} \rangle, \quad (3.1)$$

$$F_{anis}(s) = \frac{1}{2} \langle (3\delta_{\sigma\nu} \delta_{\tau\varrho} - \delta_{\sigma\tau} \delta_{\nu\varrho}) \sum_{pq} \alpha_{\sigma\tau}^{(p)} \alpha_{\nu\varrho}^{(q)*} e^{-i\mathbf{s} \cdot \mathbf{r}_{pq}} \rangle. \quad (3.2)$$

For further discussion it is convenient to refer the tensor  $\alpha_{\sigma\tau}^{(p)}$  (and, similarly,  $\alpha_{\nu\varrho}^{(q)}$ ) to the molecular system  $(x_i^{(p)})_{i=1,2,3}$  attached to the  $p$ -th (or, respectively,  $q$ -th) molecule of the medium. Thus, we have the following transformation formulas:

$$\alpha_{\sigma\tau}^{(p)} = \omega_{\sigma i}^{(p)} \omega_{\tau j}^{(p)} \alpha_{ij}^{(p)}, \quad \alpha_{\nu\varrho}^{(q)} = \omega_{\nu k}^{(q)} \omega_{\varrho l}^{(q)} \alpha_{kl}^{(q)}; \quad (3.3)$$

in the case under consideration, the fixed  $(X_{\sigma})_{\sigma=1,2,3}$  and molecular  $(x_i^{(p)})_{i=1,2,3}$  systems being rectangular ones, the transformation coefficients  $\omega_{\sigma i}^{(p)}, \dots, \omega_{\varrho l}^{(q)}$  have the meaning of the cosines of the angles subtended by the axes of these systems. The cosines satisfy the general relationship

$$\delta_{\sigma\nu} \omega_{\sigma i}^{(p)} \omega_{\nu k}^{(q)} = \omega_{\sigma i}^{(p)} \omega_{\sigma k}^{(q)} = \begin{cases} \delta_{ik} & \text{for } p = q, \\ \omega_{ik}^{(pq)} & \text{for } p \neq q, \end{cases} \quad (3.4)$$

$\omega_{ik}^{(pq)}$  denoting the cosine of the angle subtended by the  $i$ -th and  $k$ -th axes of the systems  $(x_i^{(p)})$  and  $(x_k^{(q)})$  attached to the  $p$ -th and  $q$ -th molecules, respectively.

The tensor  $\alpha_{ij}^{(p)}$  determines the constant polarizability of the isolated molecule, i. e. the polarizability independent of intermolecular fields. In optically inactive substances and throughout spectral ranges widely remote from those in which absorption appears, the tensor  $\alpha_{ij}^{(p)}$  is symmetrical and real.

If all the scattering molecules present within the volume  $V$  are of one kind  $\alpha_{ij}^{(p)} = \alpha_{ij}^{(q)} = \alpha_{ij}$ , then, by (3.3) and (3.4), eqs. (3.1) and (3.2) may be rewritten as follows:

$$F_{is}(s) = \left\langle \alpha_{ii} \alpha_{jj} \sum_{pq} \frac{\sin sr_{pq}}{sr_{pq}} \right\rangle, \quad (3.5)$$

$$I'_{anis}(s) = \frac{1}{2} \left\langle \alpha_{ij} \alpha_{kl} \sum_{pq} (3\omega_{ik}^{(pq)} \omega_{jl}^{(pq)} - \delta_{ij} \delta_{kl}) \frac{\sin sr_{pq}}{sr_{pq}} \right\rangle, \quad (3.6)$$

wherein

$$s = \frac{2\pi}{\lambda} |\mathbf{s}_0 - \mathbf{s}'| = \frac{4\pi}{\lambda} \sin \frac{\vartheta}{2}; \quad (3.7)$$

$\vartheta$  denotes the angle between the direction of propagation  $\mathbf{s}_0$  of the incident wave and that of the scattered wave  $\mathbf{s}'$ , and is termed the angle of scattering.

*Isotropic light scattering.* With the radial correlation function  $g(r)$  introduced into the theory of X-ray scattering by Zernike and Prins (1927), eq. (3.5) yields

$$F_{is}(s) = \alpha_{ii} \alpha_{jj} N \left\{ 1 + 4\pi \int \frac{\sin sr}{sr} \left[ g(r) - \frac{N}{V} \right] r^2 dr \right\}, \quad (3.8)$$

wherein  $g(r) 4\pi r^2 dr$  is the probability for the presence of a molecule within the volume element  $4\pi r^2 dr$  at a distance  $r$  from the molecule whose position is fixed.

If the linear dimensions of the scattering molecules are small as compared to the light wave-length  $\lambda$ , we have<sup>1</sup>

$$\frac{\sin sr}{sr} = 1 - \frac{1}{6} (sr)^2 + \dots \propto 1, \text{ for } \lambda \gg r, \quad (3.9)$$

and eq. (3.8) may now be written as follows:

$$F_{is} = 9\alpha^2 N \left\{ 1 + 4\pi \int_0^\infty \left[ g(r) - \frac{N}{V} \right] r^2 dr \right\}, \quad (3.10)$$

with

$$\alpha = \frac{1}{3} \alpha_{ii} = \frac{1}{3} (\alpha_{11} + \alpha_{22} + \alpha_{33}) \quad (3.11)$$

<sup>1</sup> For values of  $r$  that are not small as compared with  $\lambda$ , a quantity similar to the factor  $F_{is}$  has been discussed in a paper by Fürth and Williams (1954).



denoting the mean polarizability of the isolated molecule. It is seen that  $F_{is}$  depends on the mean polarizability of the molecules  $\alpha$  and on a quantity determining the *radial* intermolecular correlations (see, Zernike and Prins 1927):

$$\gamma_R = 1 + 4\pi \int_0^\infty \left[ g(r) - \frac{N}{V} \right] r^2 dr = \frac{N}{V} kT\beta_T, \quad (3.12)$$

wherein

$$\beta_T = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T \quad (3.13)$$

is the isothermal compressibility coefficient of the medium.

Smoluchowski (1908) and Einstein (1910) showed that the quantity  $\gamma_R$  accounts for the light scattering resulting from spontaneous density fluctuations in the medium. As both  $\alpha$  and  $\gamma_R$  are isotropic quantities,  $F_{is}$  determines *isotropic* scattering only.

*Anisotropic light scattering.* If the scattering molecules are small in terms of the light wave-length, then, with respect to (3.9), eq. (3.6) yields

$$F_{anis} = \frac{1}{2} \alpha_{ij} \alpha_{kl} \left\langle \sum_{pq} (3\omega_{ik}^{(pq)} \omega_{jl}^{(pq)} - \delta_{ij} \delta_{kl}) \right\rangle. \quad (3.14)$$

It is seen that the factor  $F_{anis}$  depends on the anisotropy of the molecules as determined by the polarizability tensor  $\alpha_{ij}$ , and on the angular intermolecular correlations determined in general by the statistical distribution of the directions of the molecular axes.

If the axes of the molecular systems coincide with the principal axes of the respective molecules, eq. (3.14) may be rewritten in the form

$$F_{anis} = \frac{1}{2} \sum_{ij} \alpha_i \alpha_j \left\langle \sum_{pq} (3 \cos^2 \Theta_{ij}^{(pq)} - 1) \right\rangle, \quad (3.15)$$

with  $\Theta_{ij}^{(pq)}$  denoting the angle between the  $i$ -th and  $j$ -th principal axes of the  $p$ -th and  $q$ -th molecules, respectively, and  $\alpha_i$  — the polarizability tensor referred to the principal axes of the molecule.

If the molecules possess the axial symmetry, the axis of symmetry being the 3-axis, then  $\alpha_1 = \alpha_2 \neq \alpha_3$ , and (3.15) yields

$$F_{anis} = \frac{1}{2} (\alpha_3 - \alpha_1)^2 \left\langle \sum_{pq} (3 \cos^2 \Theta^{(pq)} - 1) \right\rangle, \quad (3.16)$$

$\Theta^{(pq)}$  denoting the angle between the axes of symmetry of the  $p$ -th and  $q$ -th molecules, and  $\alpha_3, \alpha_1$  — the polarizabilities of the molecule in the two principal directions parallel and perpendicular to its axis of symmetry.

If, in particular, the molecules exhibit the spherical symmetry,  $\alpha_3 = \alpha_1$  and, by eq. (3.16),  $F_{anis} = 0$ . This means that  $F_{anis}$  determines the *anisotropic* light scattering only. The latter arises chiefly from the anisotropy of the molecules and from the angular intermolecular correlations.

*Light scattering in ideal gases.* In ideal gases, the molecules are mutually independent and may assume all possible configurations within the volume  $V$ . Since now  $\exp \left\{ -\frac{U(\tau)}{kT} \right\} = 1$ , the statistical mean value  $\langle \rangle$  of eq. (2.16) reduces to the isotropical average. As shown by Smoluchowski (1908), the density fluctuations in an ideal gas yield  $\gamma_R = 1$ , so that eq. (3.10) assumes the form

$$F_{\text{gas}} = 9 \alpha^2 N. \quad (3.17)$$

The factor  $F_{\text{anis}}$  as determined by eq. (3.14) may now be expanded as follows:

$$F_{\text{gas}} F_{\text{anis}} = \frac{1}{2} \alpha_{ij} \alpha_{kl} N \left\{ 3 \delta_{ik} \delta_{jl} - \delta_{ij} \delta_{kl} + \sum_{q \neq p} (3 \overline{\omega_{ik}^{(pq)}} \overline{\omega_{jl}^{(pq)}} - \delta_{ij} \delta_{kl}) \right\}; \quad (3.18)$$

with respect to

$$\overline{\omega_{ik}^{(pq)}} \overline{\omega_{jl}^{(pq)}} = \frac{1}{3} \delta_{ij} \delta_{kl}, \text{ for } p \neq q, \quad (3.19)$$

we finally obtain

$$F_{\text{gas}} F_{\text{anis}} = \frac{1}{2} (3 \alpha_{ij}^2 - \alpha_{ii}^2) N. \quad (3.20)$$

In ideal gases, the anisotropic scattering depends only on the anisotropy of the isolated molecules, whereas isotropic scattering depends on their mean polarizability.

*Factor accounting for angular intermolecular correlations.* Eq. (3.16) may be written as follows:

$$F_{\text{anis}} = (\alpha_3 - \alpha_1)^2 N R_{CM}; \quad (3.21)$$

the quantity

$$R_{CM} = \frac{1}{2N} \left\langle \sum_{pq} (3 \cos^2 \Theta^{(pq)} - 1) \right\rangle \quad (3.22)$$

appearing therein is termed *angular intermolecular correlation factor*, if the molecules possess the axial symmetry. A factor  $R_{CM}$  of the same form also appears in the theory of molecular orientational effects (cf. Buckingham 1955, and Piekara and Kielich 1957, 1958). For an ideal gas  $U(\tau) = 0$ , and eq. (3.22) yields:

$$R_{CM} = 1 + \frac{1}{2} \sum_{q \neq p} (3 \overline{\cos^2 \Theta^{(pq)}} - 1) = 1. \quad (3.23)$$

The correlation factor (3.22) accounts for the angular interaction of the molecules entering molecular assemblies which coalesce and disappear continually within the medium; such assemblies present a momentary axis of maximum polarizability arising statistically from the effect of ordering of the molecular axes. From the foregoing formulas it is seen that in an assembly of mutually „coupled“ molecules light scattering differs from that resulting from free molecules, for which  $R_{CM} = 1$ .

For instance, for the case of molecules entering aggregates of two,  $R_{CM}$  as first computed by Piekara (1939, 1950) is given by

$$R_{CM} = 2 - 3 \frac{L}{y}, \quad (3.24)$$

wherein  $L = L(\gamma)$  is the well-known Langevin function and  $\gamma = \frac{W}{kT}$  — the energy of dipole coupling in  $kT$  units. This refers to nitrobenzene, for which  $R_{CM}$  as calculated according to eq. (3.14) for the Cotton-Mouton effect (hence the indices  $CM$ ) fits well with the experimental data. It is of interest that  $R_{CM}$  for  $\gamma \neq 0$  is always larger than unity.

Anselm (1947), and Benoit and Stockmayer (1956) introduced the correlation function  $g(r, \omega)$  into the theory of the degree of depolarisation of scattered light; this function has the properties of the radial distribution function  $g(r)$  of Zernike and Prins (1927) as generalized for orientational correlations of the molecules. With the function  $g(r, \omega)$ , the correlation factor (3.22) takes the form

$$R_{CM} = 1 + 2\pi \int_r \int_\omega (3 \cos^2 \Theta - 1) \left[ g(r, \omega) - \frac{N}{4\pi V} \right] r^2 dr d\omega, \quad (3.25)$$

wherein  $\Theta$  is the angle subtended by the axis of symmetry of a given molecule and that of an arbitrary one at distance  $r$ .

#### 4. Optical Anisotropy and Degree of Depolarisation of Scattered Light

*Optical anisotropy.* The ratio of  $F_{\text{anis}}$  and  $F_{\text{is}}$  which determine, respectively, anisotropic and isotropic light scattering, i. e.

$$\Delta^2 \equiv \frac{F_{\text{anis}}}{F_{\text{is}}}, \quad (4.1)$$

yields a measure of the optical anisotropy of the scattering medium.

Substituting herein the expressions of eqs. (3.10) and (3.14), we have

$$\Delta^2 = \frac{\alpha_{ij} \alpha_{kl} \langle \sum_{pq} (3\omega_{ik}^{(pq)} \omega_{jl}^{(pq)} - \delta_{ij} \delta_{kl}) \rangle}{2\alpha_{ii} \alpha_{jj} N \left\{ 1 + 4\pi \int_0^\infty \left[ g(r) - \frac{N}{V} \right] r^2 dr \right\}}; \quad (4.2)$$

this is an expression yielding a measure of the optical anisotropy of a liquid consisting of molecules of arbitrary symmetry.

Hence, for ideal gases, we have  $_{\text{gas}}\Delta^2 = \delta_\alpha^2$ , wherein  $\delta_\alpha$  is the optical anisotropy of an isolated molecule

$$\delta_\alpha^2 = \frac{3\alpha_{ij} \alpha_{ij} - \alpha_{ii} \alpha_{jj}}{2\alpha_{ii} \alpha_{jj}}, \quad (4.3)$$

or, if the polarizability tensor be referred to the principal axes of the molecule,

$$\delta_\alpha^2 = \frac{(\alpha_1 - \alpha_2)^2 + (\alpha_2 - \alpha_3)^2 + (\alpha_3 - \alpha_1)^2}{2(\alpha_1 + \alpha_2 + \alpha_3)^2}. \quad (4.4)$$

For molecules having the axial symmetry the foregoing expression reduces to

$$\delta_a^2 = \left( \frac{\alpha_3 - \alpha_1}{\alpha_3 + 2\alpha_1} \right)^2 = \left( \frac{\alpha_3 - \alpha_1}{3\alpha} \right)^2; \quad (4.5)$$

clearly, for spherically symmetrical molecules  $\delta_a = 0$ .

In condensed gases and liquids whose molecules have the axial symmetry, eq. (4.1) yields, with respect to (3.10) and (3.21):

$$\Delta^2 = \delta_a^2 \frac{R_{CM}}{\gamma_R}; \quad (4.6)$$

this means that the optical anisotropy of condensed gases and liquids depends on that of the isolated molecule,  $\delta_a$ , and on the ratio of the orientational ( $R_{CM}$ ) and radial ( $\gamma_R$ ) correlations.

Introducing  $R_{CM}$  from (3.25) into eq. (4.6), we obtain the Benoit-Stockmayer (1956) formula:

$$\Delta^2 = \frac{\delta_a^2 V}{Nk T \beta_T} \left\{ 1 + 2\pi \int_r \int_\omega (3 \cos^2 \Theta - 1) \left[ g(r, \omega) - \frac{N}{4\pi V} \right] r^2 dr d\omega \right\}; \quad (4.7)$$

the latter has since been generalized by Benoit and Weill (1956) and by Weill (1958) for dilute solutions of liquids.

*Depolarisation ratio of scattered light.* In a medium exhibiting anisotropic scattering ( $F_{\text{anis}} \neq 0$ ), the light scattered undergoes depolarisation. The degree of depolarisation is usually defined as the ratio of the lowest ( $I_{\text{min}}$ ) and highest ( $I_{\text{max}}$ ) possible values of the scattered intensity (see, Born 1933):

$$D \equiv \frac{I_{\text{min}}}{I_{\text{max}}}, \quad (4.8)$$

$I_{\text{min}}$  and  $I_{\text{max}}$  being computed from the fundamental equation (2.18).

If the light beam incident on the scattering medium is not polarized and if the light scattered is observed with a Nicol prism, we have

$$\cos \Omega_{en} = \cos \varphi_e \cos \varphi_n + \sin \varphi_e \sin \varphi_n \cos \vartheta; \quad (4.9)$$

the angles  $\varphi_e$ ,  $\varphi_n$  and  $\vartheta$  are explained in Fig. 1. In the case under consideration, the fundamental equation (2.18) should be averaged over all directions of the electric vector  $\mathbf{E}$  in the plane perpendicular to the propagation direction of the incident wave, i. e. to the vector  $\mathbf{S}_o$ . This is equivalent to averaging over  $\varphi_e$  from 0 to  $2\pi$ :

$$I(\varphi_n, \vartheta) = 2 \cdot \frac{1}{2\pi} \int_0^{2\pi} I_n d\varphi_e, \quad (4.10)$$

which yields, by (4.9),

$$I(\varphi_n, \vartheta) = Q \{ 5 (1 - \sin^2 \varphi_n \sin^2 \vartheta) F_{is}(s) + (7 - \sin^2 \varphi_n \sin^2 \vartheta) F_{\text{anis}}(s) \}. \quad (4.11)$$



When the nicol is rotated, the scattered intensity transmitted attains its maximum value with the former transmitting vibrations parallel to the plane of the incident light vector  $\mathbf{E}$  only, i. e. at  $\varphi_n = 0$ . The minimum scattered intensity is observed when the nicol is set so as to transmit vibrations perpendicular to the plane of  $\mathbf{E}$ , i. e. at

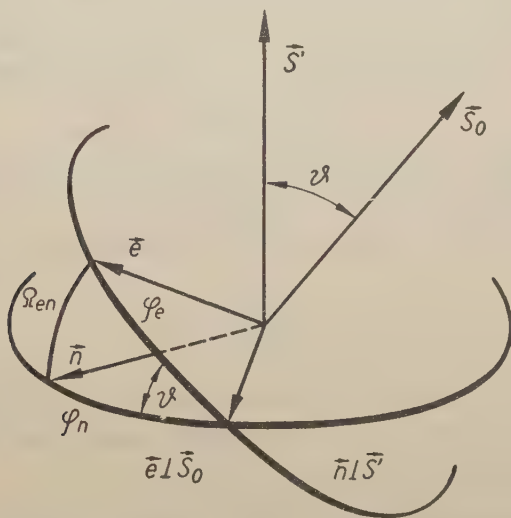


Fig. 1. Space arrangement of the unit vectors  $\vec{s}_0$  and  $\vec{s}$  in the direction of the incident and scattered light beams, and of unit electric vectors  $\vec{e}$  and  $\vec{n}$  in either light beam, respectively.

$\varphi_n = 90^\circ$ . Thus, by the definition of eq. (4.8) and with respect to (4.11), a general expression for the degree of depolarisation of light scattered by an isotropic medium is obtained as follows:

$$D(\vartheta) = \frac{5 \cos^2 \vartheta F_{\text{is}}(s) + (6 + \cos^2 \vartheta) F_{\text{anis}}(s)}{5 F_{\text{is}}(s) + 7 F_{\text{anis}}(s)}, \quad (4.12)$$

When observation of the light scattered is carried out at an angle of  $90^\circ$  with respect to the direction of incidence and if the scattering medium satisfies the condition of eq. (3.9), the following relation is obtained for  $\vartheta = 90^\circ$ :

$$D(90^\circ) \equiv D = \frac{6 F_{\text{anis}}}{5 F_{\text{is}} + 7 F_{\text{anis}}}. \quad (4.13)$$

The degree of depolarisation  $D$  thus defined is related to

$$D' = \frac{3 F_{\text{anis}}}{5 F_{\text{is}} + 4 F_{\text{anis}}}, \quad (4.14)$$

the degree of depolarisation for plane polarized incident light, by the formula

$$D = \frac{2D'}{1 + D'}. \quad (4.15)$$

The formula (4.13) (or (4.14)) together with expressions (2.22) and (2.23) is identical with the one derived by Buckingham and Stephen (1957) in their theory of the degree of depolarisation of light scattered by a dense medium.

*Degree of depolarisation in some special cases.* Substituting  $F_{is}$  and  $F_{anis}$ , as given by (3.10) and (3.14), in the general expression (4.13), an expression for the degree of depolarisation of light in condensed gases and liquids possessing molecules of arbitrary symmetry is obtained (Kielich 1958a, Piekara and Kielich 1958):

$$D = \frac{6 \alpha_{ij} \alpha_{kl} \langle \sum_{pq} (3 \omega_{ik}^{(pq)} \omega_{jl}^{(pq)} - \delta_{ij} \delta_{kl}) \rangle}{10 \alpha_{ii} \alpha_{jj} N \gamma_R + 7 \alpha_{ij} \alpha_{kl} \langle \sum_{pq} (3 \omega_{ik}^{(pq)} \omega_{jl}^{(pq)} - \delta_{ij} \delta_{kl}) \rangle}. \quad (4.16)$$

For substances whose molecules exhibit the axial symmetry, (4.16) reduces to

$$D = \frac{6 \delta_\alpha^2 R_{CM}}{5 \gamma_R + 7 \delta_\alpha^2 R_{CM}}, \quad (4.17)$$

where  $\delta_\alpha = (\alpha_3 - \alpha_1) / 3\alpha$ , and  $R_{CM}$  is given by (3.22). If the angular correlation factor  $R_{CM}$  is given by (3.25), the eq. (4.17) is identical with the result obtained by Anselm (1947), and Benoit and Stockmayer (1956).

For an ideal gas, (4.16) yields the Gans-Cabannes formula:

$$D_{\text{gas}} = \frac{6 (3 \alpha_{ij} \alpha_{ij} - \alpha_{ii} \alpha_{jj})}{10 \alpha_{ii} \alpha_{jj} + 7 (3 \alpha_{ij} \alpha_{ij} - \alpha_{ii} \alpha_{jj})} = \frac{6 \delta_\alpha^2}{5 + 7 \delta_\alpha^2}. \quad (4.18)$$

For a substance whose molecules possess the spherical symmetry,  $\delta_\alpha = 0$ , and the degree of depolarisation assumes the value zero, which means that in such a medium light undergoes no depolarization.

### 5. Rayleigh's Ratio and Coefficient of Extinction

*Rayleigh's ratio.* With an incident beam of natural light, and if observation is carried out without a nicol, eq. (4.11) should, additionally, be averaged over all values of  $\varphi_n$  from 0 to  $2\pi$ , thus

$$I(\vartheta) = \frac{1}{2\pi} \int_0^{2\pi} I(\varphi_n, \vartheta) d\varphi_n; \quad (5.1)$$

hence, with respect to (4.11),

$$I(\vartheta) = \frac{1}{2} Q \{ 5 (1 + \cos^2 \vartheta) F_{is}(s) + (13 + \cos^2 \vartheta) F_{anis}(s) \}. \quad (5.2)$$

The scattering constant, also known as Rayleigh's ratio, is defined as follows:

$$S(\vartheta) \equiv \frac{I(\vartheta)}{I_0} \frac{R_0^2}{V}; \quad (5.3)$$

by (5.2), the following general expression for Rayleigh's ratio is obtained

$$S(\vartheta) = \frac{1}{90V} \left( \frac{2\pi}{\lambda} \right)^4 \left( \frac{n^2 + 2}{3} \right)^2 \{ 5(1 + \cos^2 \vartheta) F_{is}(s) + (13 + \cos^2 \vartheta) F_{anis}(s) \}. \quad (5.4)$$

If observation is at an angle of  $90^\circ$  with respect to the direction of incidence ( $\vartheta = 90^\circ$ ) and if eq. (3.9) is satisfied, the foregoing expression reduces to

$$S(90^\circ) \equiv S = \frac{1}{90V} \left( \frac{2\pi}{\lambda} \right)^4 \left( \frac{n^2 + 2}{3} \right)^2 (5 F_{is} + 13 F_{anis}). \quad (5.5)$$

*Extinction coefficient.* In passing through the medium, the intensity of the light beam diminishes as a result of scattering (the effect of absorption is neglected here). On emerging from a layer of thickness  $l$ , the intensity is given by the well-known Lambert law

$$I_l = I_0 e^{-hl}, \quad (5.6)$$

wherein  $h$  is a coefficient dependent on the properties of the medium and on the light wave-length  $\lambda$ , and determines the weakening of a beam of intensity  $I_0$  resulting from scattering. By definition (see, Cabannes 1929),

$$h = \int_0^{2\pi} \int_0^\pi S(\vartheta) \sin \vartheta d\vartheta d\varphi, \quad (5.7)$$

i. e. by (5.4), a general expression for the coefficient of extinction (turbidity) is hence derived:

$$h = \frac{\pi}{45V} \left( \frac{2\pi}{\lambda} \right)^4 \left( \frac{n^2 + 2}{3} \right)^2 \int_0^\pi \{ 5(1 + \cos^2 \vartheta) F_{is}(s) + (13 + \cos^2 \vartheta) F_{anis}(s) \} \sin \vartheta d\vartheta, \quad (5.8)$$

wherein  $F_{is}(s)$  and  $F_{anis}(s)$  are given by eqs. (2.22) and (2.23).

In particular, for small molecules, i. e. if the condition of eq. (3.9) is satisfied, the foregoing equation yields

$$h = \frac{8\pi}{27V} \left( \frac{2\pi}{\lambda} \right)^4 \left( \frac{n^2 + 2}{3} \right)^2 (F_{is} + 2 F_{anis}). \quad (5.9)$$

*S and h for special cases.* Substituting  $F_{is}$  and  $F_{anis}$  from eqs. (3.10) and (3.14) in eqs. (5.5) and (5.9), the following expression is obtained for real gases and liquids consisting of molecules of arbitrary symmetry:

$$S = \frac{1}{18} \left( \frac{2\pi}{\lambda} \right)^4 \left( \frac{n^2 + 2}{3} \right)^2 \frac{N}{V} \alpha_{ij} \alpha_{kl} \left\{ \delta_{ij} \delta_{kl} \left[ 1 + 4\pi \int_0^\infty \left( g - \frac{N}{V} \right) r^2 dr \right] + \right. \\ \left. + \frac{13}{10N} \left\langle \sum_{pq} (3 \omega_{ik}^{(pq)} \omega_{jl}^{(pq)} - \delta_{ij} \delta_{kl}) \right\rangle \right\}, \quad (5.10)$$

$$h = \frac{8\pi}{27} \left( \frac{2\pi}{\lambda} \right)^4 \left( \frac{n^2 + 2}{3} \right)^2 \frac{N}{V} \alpha_{ij} \alpha_{kl} \left\{ \delta_{ij} \delta_{kl} \left[ 1 + 4\pi \int_0^\infty \left( g - \frac{N}{V} \right) r^2 dr \right] + \right. \\ \left. + \frac{1}{N} \left\langle \sum_{pq} (3 \omega_{ik}^{(pq)} \omega_{jl}^{(pq)} - \delta_{ij} \delta_{kl}) \right\rangle \right\}. \quad (5.11)$$

If the tensor of optical polarizability be referred to the principal axes of the molecule, these equations yield:

$$S = \frac{1}{18} \left( \frac{2\pi}{\lambda} \right)^4 \left( \frac{n^2 + 2}{3} \right)^2 \frac{N}{V} \sum_{i,j=1}^3 \alpha_i \alpha_j \left\{ \gamma_R + \frac{13}{10N} \left\langle \sum_{pq} (3 \cos^2 \Theta_{ij}^{(pq)} - 1) \right\rangle \right\}, \quad (5.12)$$

$$h = \frac{8\pi}{27} \left( \frac{2\pi}{\lambda} \right)^4 \left( \frac{n^2 + 2}{3} \right)^2 \frac{N}{V} \sum_{i,j=1}^3 \alpha_i \alpha_j \left\{ \gamma_R + \frac{1}{N} \left\langle \sum_{pq} (3 \cos^2 \Theta_{ij}^{(pq)} - 1) \right\rangle \right\}. \quad (5.13)$$

With the Lorentz-Lorenz formula

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3} \frac{N}{V} \alpha, \quad (5.14)$$

and for molecules having the axial symmetry, eqs. (5.12) and (5.13) reduce to

$$S = \frac{\pi^2 (n^2 - 1)^2 V}{2 \lambda^4 N} \left( \gamma_R + \frac{13}{5} \delta_a^2 R_{CM} \right), \quad (5.15)$$

$$h = \frac{8\pi^3 (n^2 - 1)^2 V}{3 \lambda^4 N} \left( \gamma_R + 2 \delta_a^2 R_{CM} \right), \quad (5.16)$$

wherein  $\delta_a$  is the optical anisotropy of an axially symmetric molecule. The formulas derived differ from the analogous King-Rocard formulas by the orientational correlation factor  $R_{CM}$  in the term accounting for anisotropy. For spherically symmetrical molecules,  $\delta_a = 0$ , and eqs. (5.15) and (5.16) assume the form of the Einstein-Smoluchowski-Rocard formulas for liquids consisting of spherical molecules:

$$S = \frac{\pi^2 (n^2 - 1)^2}{2 \lambda^4} kT \beta_T, \quad h = \frac{8\pi^3 (n^2 - 1)^2}{3 \lambda^4} kT \beta_T. \quad (5.17)$$

For an ideal gas, by (4.3) and with the Lorentz-Lorenz equation, eqs. (5.10) and (5.11) yield the Born-Cabannes formulas:

$$S_{\text{gas}} = \frac{\pi^2 (n^2 - 1)^2 V}{2 \lambda^4 N} \left( 1 + \frac{13}{5} \delta_a^2 \right), \quad (5.18)$$

$$h_{\text{gas}} = \frac{8\pi^3 (n^2 - 1)^2 V}{3 \lambda^4 N} (1 + 2 \delta_a^2). \quad (5.19)$$



For an ideal gas consisting of spherical molecules the Born-Cabannes formulas reduce to the well-known formulas given by Rayleigh:

$$_{\text{gas}}S = \frac{2\pi^2 (n-1)^2 V}{\lambda^4 N}, \quad _{\text{gas}}h = \frac{32\pi^3 (n-1)^2 V}{3\lambda^4 N}. \quad (5.20)$$

## 6. Second Virial Coefficients for Light Scattering in Compressed Gases

*General form of virial coefficients.* Virial coefficients have been computed by Harris and Alder (1953) and by Buckingham and Pople (1955) in the theory of electric polarisation, and by Buckingham (1955) in that of Kerr's effect. The virial coefficients for light scattering in compressed gases will now be computed by the method of the latter authors. For this, the molecular factors  $F_{\text{is}}(s)$  and  $F_{\text{anis}}(s)$  given by eqs (2.22) and (2.23) are expanded in powers of  $1/V$ :

$$F_{\text{is}}(s) = A_S^{\text{is}} + \frac{B_S^{\text{is}}}{V} + \frac{C_S^{\text{is}}}{V^2} + \dots, \quad (6.1)$$

$$F_{\text{anis}}(s) = A_S^{\text{anis}} + \frac{B_S^{\text{anis}}}{V} + \frac{C_S^{\text{anis}}}{V^2} + \dots; \quad (6.2)$$

the coefficients  $A_S^{\text{is}}$ ,  $A_S^{\text{anis}}$ ,  $B_S^{\text{is}}$ ,  $B_S^{\text{anis}}$ ,  $C_S^{\text{is}}$ ,  $C_S^{\text{anis}}$ , ... are termed the first, second, third, ... virial coefficient of isotropic ( $F_{\text{is}}$ ) and anisotropic ( $F_{\text{anis}}$ ) light scattering, respectively.

The first virial coefficients are defined as follows:

$$A_S^{\text{is}} = \lim_{V \rightarrow \infty} F_{\text{is}}(s), \quad A_S^{\text{anis}} = \lim_{V \rightarrow \infty} F_{\text{anis}}(s); \quad (6.3)$$

by (2.22) and (2.23) we have

$$A_S^{\text{is}} = 9\alpha^2 N, \quad A_S^{\text{anis}} = 9\alpha^2 \delta_a^2 N, \quad (6.4)$$

wherein  $\alpha$  is the mean polarizability of the isolated molecule, and  $\delta_a$  denotes its anisotropy as given in general form by eq. (4.3). Comparison with eqs. (3.17) and (3.20) shows that the first virial coefficients  $A_S^{\text{is}}$  and  $A_S^{\text{anis}}$  account for light scattering by free molecules ("gas molecules").

By definition, the second virial coefficients are given by

$$B_S^{\text{is}} = \lim_{V \rightarrow \infty} \{[F_{\text{is}}(s) - A_S^{\text{is}}] V\}, \quad (6.5)$$

$$B_S^{\text{anis}} = \lim_{V \rightarrow \infty} \{[F_{\text{anis}}(s) - A_S^{\text{anis}}] V\}; \quad (6.6)$$

by (2.22), (2.23) and (6.4), they may be written in the following general form:

$$B_S^{\text{is}} = \lim_{V \rightarrow \infty} \left\{ \left\langle \delta_{\sigma\tau} \delta_{\nu\varrho} \sum_{pq} \frac{\partial m_{\sigma}^{\prime(p)}}{\partial E_{\tau}^{(p)}} \left( \frac{\partial m_{\nu}^{\prime(q)}}{\partial E_{\varrho}^{(q)}} \right)^* e^{-i\mathbf{s} \cdot \mathbf{r}_{pq}} - 9\alpha^2 N \right\rangle V \right\}, \quad (6.7)$$

$$B_S^{\text{anis}} = \lim_{V \rightarrow \infty} \left\{ \left\langle \frac{1}{2} (3\delta_{\sigma\nu} \delta_{\tau\varrho} - \delta_{\sigma\tau} \delta_{\nu\varrho}) \sum_{pq} \frac{\partial m_{\sigma}^{\prime(p)}}{\partial E_{\tau}^{(p)}} \left( \frac{\partial m_{\nu}^{\prime(q)}}{\partial E_{\varrho}^{(q)}} \right)^* e^{-i\mathbf{s} \cdot \mathbf{r}_{pq}} - 9\alpha^2 \delta_{\alpha}^2 N \right\rangle V \right\}. \quad (6.8)$$

As the second virial coefficients contain only contributions accounting for the interaction of molecules in pairs, eqs. (6.7) and (6.8) may be rewritten as follows

$$B_S^{\text{is}} = \frac{4\pi N^2}{\Omega} \int_{\mathbf{r}} \int_{\omega} \left\{ \frac{\partial m_{\sigma}^{\prime(1)}}{\partial E_{\sigma}^{(1)}} \left( \frac{\partial m_{\tau}^{\prime(2)}}{\partial E_{\tau}^{(2)}} + \frac{\partial m_{\tau}^{\prime(2)}}{\partial E_{\tau}^{(2)}} \right)^* - 9\alpha^2 \right\} e^{-\frac{U_{12}}{kT}} r^2 dr d\omega, \quad (6.9)$$

$$B_S^{\text{anis}} = \frac{2\pi N^2}{\Omega} \int_{\mathbf{r}} \int_{\omega} \left\{ (3\delta_{\sigma\nu} \delta_{\tau\varrho} - \delta_{\sigma\tau} \delta_{\nu\varrho}) \frac{\partial m_{\sigma}^{\prime(1)}}{\partial E_{\tau}^{(1)}} \left( \frac{\partial m_{\nu}^{\prime(2)}}{\partial E_{\varrho}^{(2)}} + \frac{\partial m_{\nu}^{\prime(2)}}{\partial E_{\varrho}^{(2)}} \right)^* - 18\alpha^2 \delta^2 \right\} e^{-\frac{U_{12}}{kT}} r^2 dr d\omega, \quad (6.10)$$

wherein  $m_{\sigma}^{\prime(1)}$ ,  $m_{\nu}^{\prime(2)}$  are the dipole moments of molecules 1 and 2,  $U_{12}$  is the potential energy of interaction between a pair of molecules, and  $\Omega = \int_{\omega} d\omega$  is the integral over all angular coordinates.

*Spherically symmetric molecules.* For simplification, assume the scattering molecules to have spherical symmetry. Then, by (6.4), the first virial coefficients are

$$A_S^{\text{is}} = 9\alpha^2 N, \quad A_S^{\text{anis}} = 0, \quad (6.11)$$

i. e., the first virial coefficient of anisotropic scattering vanishes.

To compute the second virial coefficients, the expansion (2.34), which accounts for the effect of the intermolecular field on the polarizability of a molecule immersed in a condensed medium, will be applied. Since for spherically symmetrical molecules the tensor  $\alpha_{ij}$  reduces to the isotropic tensor  $\alpha_{ij} = \alpha \delta_{ij}$ , and with respect to expansion (2.34) and condition (3.9), eqs. (6.9) and (6.10) yield

$$B_S^{\text{is}} = 36\pi\alpha^2 N^2 \int_{\mathbf{r}} \left\{ 1 + 8 \frac{\alpha^2}{r^6} + 8 \frac{\alpha^3}{r^3} + 32 \frac{\alpha^4}{r^{12}} + \dots \right\} e^{-\frac{U(r)}{kT}} r^2 dr, \quad (6.12)$$

$$B_S^{\text{anis}} = 72\pi\alpha^2 N^2 \int_{\mathbf{r}} \left\{ \frac{\alpha^2}{r^6} + 2 \frac{\alpha^3}{r^9} + 7 \frac{\alpha^4}{r^{12}} + \dots \right\} e^{-\frac{U(r)}{kT}} r^2 dr. \quad (6.13)$$

Pople (1954), assuming  $U(r)$  in the form of the Lennard-Jones potential (2.36), proved that

$$\int_0^{\infty} r^{-n} e^{-\frac{U(r)}{kT}} r^2 dr = \frac{r_0^{3-n}}{12} \gamma^{-4} H_n(\gamma), \quad (6.14)$$

wherein

$$H_n(\gamma) = \gamma^{\frac{27-n}{6}} \sum_{m=0}^{\infty} \Gamma\left(\frac{6m+n-3}{12}\right) \frac{\gamma^m}{m!}, \quad (6.15)$$

with  $\gamma = 2 \left( \frac{\varepsilon^*}{kT} \right)^{\frac{1}{2}}$ . The functions  $H_n(\gamma)$  have been discussed and their values tabulated by Buckingham and Pople (1955b).

With eq. (6.14), we obtain finally from (6.12) and (6.13)

$$B_S^{\text{is}} = 9\alpha^2 NV(\gamma_R - 1) + \frac{24\pi\alpha^4 N^2}{r_0^3 \gamma^4} \left\{ H_6(\gamma) + \frac{\alpha}{r_0^3} H_9(\gamma) + 4 \frac{\alpha^2}{r_0^6} H_{12}(\gamma) + \dots \right\}, \quad (6.16)$$

$$B_S^{\text{anis}} = \frac{6\pi\alpha^4 N^2}{r_0^3 \gamma^4} \left\{ H_6(\gamma) + 2 \frac{\alpha}{r_0^3} H_9(\gamma) + 7 \frac{\alpha^2}{r_0^6} H_{12}(\gamma) + \dots \right\}, \quad (6.17)$$

wherein  $\gamma_R$  is defined in analogy with (3.12).

Thus, in compressed gases consisting of spherical molecules,  $A_S^{\text{is}} \neq 0$ ,  $B_S^{\text{is}} \neq 0$  and  $A_S^{\text{anis}} = 0$ , whilst  $B_S^{\text{anis}} \neq 0$ . This means that free spherical molecules give rise to isotropic light scattering in a medium. However, in compressed gases, intermolecular forces cause the spherical molecules to form assemblies, which represent anisotropic scattering centres for the incident light beam. It is seen from eq. (6.17) that even the presence of assemblies consisting of no more than two spherical molecules is sufficient for the medium to exhibit additional, anisotropic scattering. Hence, on passing through such a medium, light may undergo depolarization.

*Axial symmetrical molecules with dipole moment.* If the anisotropic molecules possess the axial symmetry, then, neglecting all terms in the higher powers of the tensor  $\alpha_{ij}$  in expansion (2.34), we may write, by (6.9) and (6.10)

$$B_S^{\text{is}} = \frac{36\pi\alpha^2 N^2}{\Omega} \int_r \int_{\omega} e^{-\frac{U_{12}}{kT}} r^2 dr d\omega, \quad (6.18)$$

$$B_S^{\text{anis}} = \frac{18\pi\alpha^2 \delta_\alpha^2 N^2}{\Omega} \int_r \int_{\omega} (3 \cos^2 \Theta^{(12)} - 1) e^{-\frac{U_{12}}{kT}} r^2 dr d\omega, \quad (6.19)$$

wherein  $\Theta^{(12)}$  is the angle subtended by the axes of symmetry of molecules 1 and 2.

Combining eqs. (2.36) and (2.37), the following expression is obtained for the potential energy of interaction of two dipole molecules (the permanent dipole-induced dipole interaction is neglected):

$$U_{12} = 4\varepsilon^* \left\{ \left( \frac{r_0}{r} \right)^{12} - \left( \frac{r_0}{r} \right)^6 \right\} - \frac{\mu^2}{r^3} (3 \cos \Theta^{(1)} \cos \Theta^{(2)} - \cos \Theta^{(12)}), \quad (6.20)$$

with  $\cos \Theta^{(12)} = \cos \Theta^{(1)} \cos \Theta^{(2)} + \sin \Theta^{(1)} \sin \Theta^{(2)} \cos(\varphi_2 - \varphi_1)$ , wherein the angles  $\Theta^{(12)}$ ,  $\Theta^{(1)}$ , ...,  $\varphi_2$  are explained in Fig. 2.

Substituting (6.20) in (6.18) and (6.19) we obtain, by (6.14),

$$B_S^{\text{is}} = 9\alpha^2 NV(\gamma_R - 1) + \frac{\pi \alpha^2 r_0^3 x^2 N^2}{16} \left\{ H_6(y) + \frac{3x^2 y^4}{400} H_{12}(y) + \dots \right\}, \quad (6.21)$$

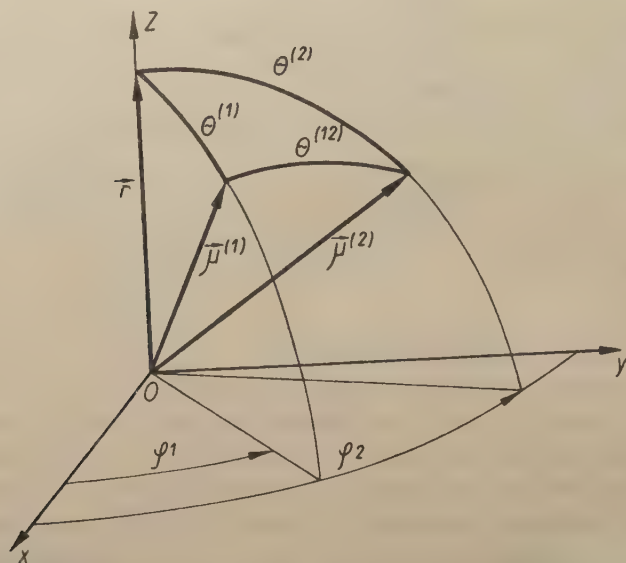


Fig. 2. Angles determining the mutual orientation of two dipoles  $\vec{\mu}^{(1)}$  and  $\vec{\mu}^{(2)}$  in the fixed system of reference  $(x, y, z)$

$$B_S^{\text{anis}} = \frac{\pi \alpha^2 \delta_a^2 r_0^3 x^2 N^2}{400} \left\{ H_6(y) + \frac{3x^2 y^4}{196} H_{12}(y) + \dots \right\}, \quad (6.22)$$

wherein  $x = \frac{\mu^2}{e^* r_0^3}$ .

The virial coefficient  $B_S^{\text{anis}}$  is related as follows to the second Kerr constant virial coefficient  $B_K$  as computed for the case under consideration by Buckingham (1955):

$$B_K = \frac{4\pi}{405 kT} \frac{a \delta_a}{\alpha \delta_a} B_S^{\text{anis}}, \quad (6.23)$$

wherein

$$\delta_a = \frac{a_3 - a_1}{3a} \quad (6.24)$$

is the electrical anisotropy of an axially symmetric molecule, and  $a = \frac{1}{3} (a_3 + 2a_1)$  — its mean polarizability in a static electric field\*).

\*) A detailed discussion of  $B_S^{\text{is}}$  and  $B_S^{\text{anis}}$  for other molecular models will be given in a subsequent paper by the author.



### 7. Effect of the Molecular Field and Hyperpolarizability of the Molecules on Light Scattering in Liquids

In a condensed medium, light scattering depends also on the molecular field and on the hyperpolarizability of the molecules (see Buckingham and Stephen 1957). In the present case, when computing the molecular factors  $F_{is}$  and  $F_{anis}$ , the tensor of the polarizability of the molecules, as given by the expansion (2.33), should be applied. The expressions of (2.22) and (2.23) may be written as follows:

$$F_{is}(s) = \left\langle \delta_{\sigma\tau} \delta_{\nu\varrho} \sum_{pq} (\alpha_{\sigma\tau}^{(p)} \alpha_{\nu\varrho}^{(q)} + V_{\sigma\tau\nu\varrho}^{(pq)}) \cos \mathbf{s} \cdot \mathbf{r}_{pq} \right\rangle, \quad (7.1)$$

$$F_{anis}(s) = \frac{1}{2} \left\langle (3\delta_{\sigma\nu} \delta_{\tau\varrho} - \delta_{\sigma\tau} \delta_{\nu\varrho}) \sum_{pq} (\alpha_{\sigma\tau}^{(p)} \alpha_{\nu\varrho}^{(q)} + V_{\sigma\tau\nu\varrho}^{(pq)}) \cos \mathbf{s} \cdot \mathbf{r}_{pq} \right\rangle, \quad (7.2)$$

wherein the tensor

$$\begin{aligned} V_{\sigma\tau\nu\varrho}^{(pq)} = & \alpha_{\sigma\tau}^{(p)} \beta_{\nu\varrho}^{(q)} F_{0\gamma}^{(q)} + \alpha_{\nu\varrho}^{(q)} \beta_{\sigma\tau}^{(p)} F_{0\gamma}^{(p)} + \beta_{\sigma\tau}^{(p)} \beta_{\nu\varrho}^{(q)} F_{0\gamma}^{(p)} F_{0\delta}^{(q)} + \\ & + \frac{1}{2} \alpha_{\sigma\tau}^{(p)} \gamma_{\nu\varrho\gamma\delta}^{(q)} F_{0\gamma}^{(q)} F_{0\delta}^{(q)} + \frac{1}{2} \alpha_{\nu\varrho}^{(q)} \gamma_{\sigma\tau\gamma\delta}^{(p)} F_{0\gamma}^{(p)} F_{0\delta}^{(p)} + \dots \\ & + (\alpha_{\sigma\alpha}^{(p)} \alpha_{\nu\beta}^{(q)} + \dots) \left( \frac{\partial F_{\alpha}^{(p)}}{\partial E_{\tau}^{(p)}} \delta_{\beta\varrho} + \delta_{\alpha\tau} \frac{\partial F_{\beta}^{(q)}}{\partial E_{\varrho}^{(q)}} + \frac{\partial F_{\alpha}^{(p)}}{\partial E_{\tau}^{(p)}} \frac{\partial F_{\beta}^{(q)}}{\partial E_{\varrho}^{(q)}} \right) \end{aligned} \quad (7.3)$$

determines the effect of the internal molecular field and hyperpolarizability of the molecules on light scattering in a condensed medium.

*Light scattering on assemblies of spherical molecules.* In order to obtain insight into the part played by the internal molecular field in the scattering of light, it will be assumed for the sake of simplicity that the condensed medium consists of assemblies of spherical molecules. Thus,  $\mu_i = \beta_{ijk} = 0$  and  $\alpha_{ij}, \gamma_{ijkl}$  reduce to the isotropic tensors given by

$$\alpha_{ij} = \alpha_{ij}, \quad \gamma_{ijkl} = \frac{1}{3} \gamma (\delta_{ij} \delta_{kl} + \delta_{ik} \delta_{jl} + \delta_{il} \delta_{kj}), \quad (7.4)$$

and the foregoing expressions yield, quite generally:

$$\begin{aligned} F_{is}(s) = & \left\langle \sum_{pq} \left\{ \alpha^2 \left( 9 + 3 \frac{\partial F_{\alpha}^{(p)}}{\partial E_{\alpha}^{(p)}} + 3 \frac{\partial F_{\beta}^{(q)}}{\partial E_{\beta}^{(q)}} + \frac{\partial F_{\alpha}^{(p)}}{\partial E_{\alpha}^{(p)}} \frac{\partial F_{\beta}^{(q)}}{\partial E_{\beta}^{(q)}} \right) + \right. \right. \\ & \left. \left. + \frac{5}{2} \alpha \gamma (F_{\sigma\alpha}^{(p)} F_{\sigma\alpha}^{(p)} + F_{\sigma\beta}^{(q)} F_{\sigma\beta}^{(q)}) + \dots \right\} \cos \mathbf{s} \cdot \mathbf{r}_{pq} \right\rangle, \end{aligned} \quad (7.5)$$

$$F_{anis}(s) = \frac{1}{2} \left\langle \sum_{pq} \left\{ \alpha^2 \left( 3 \frac{\partial F_{\alpha}^{(p)}}{\partial E_{\beta}^{(p)}} \frac{\partial F_{\alpha}^{(q)}}{\partial E_{\beta}^{(q)}} - \frac{\partial F_{\alpha}^{(p)}}{\partial E_{\alpha}^{(p)}} \frac{\partial F_{\beta}^{(q)}}{\partial E_{\beta}^{(q)}} \right) + \dots \right\} \cos \mathbf{s} \cdot \mathbf{r}_{pq} \right\rangle. \quad (7.6)$$

If  $\lambda \gg r$ , the foregoing relations yield a general expression for the optical anisotropy  $\Delta^2$  of a condensed medium consisting of spherical molecules:

$$\Delta^2 = \frac{\left\langle \sum_{pq} \left( 3 \frac{\partial F_{\alpha}^{(p)}}{\partial E_{\beta}^{(p)}} \frac{\partial F_{\alpha}^{(q)}}{\partial E_{\beta}^{(q)}} - \frac{\partial F_{\alpha}^{(p)}}{\partial E_{\alpha}^{(p)}} \frac{\partial F_{\beta}^{(q)}}{\partial E_{\beta}^{(q)}} \right) \right\rangle}{2 \left\langle \sum_{pq} \left( 9 + 3 \frac{\partial F_{\alpha}^{(p)}}{\partial E_{\alpha}^{(p)}} + 3 \frac{\partial F_{\beta}^{(q)}}{\partial E_{\beta}^{(q)}} + \frac{\partial F_{\alpha}^{(p)}}{\partial E_{\alpha}^{(p)}} \frac{\partial F_{\beta}^{(q)}}{\partial E_{\beta}^{(q)}} \right) \right\rangle}. \quad (7.7)$$

Hence, it is clearly seen that the optical anisotropy of such a medium arises from *fluctuations of the molecular field*. If the internal molecular field  $F_{\alpha}^{(p)}$  is here assumed to be given by the expansion (2.29), which, in the case of spherical molecules, takes the form

$$F_{\alpha}^{(p)} = F_{0\alpha}^{(p)} - \alpha \sum_r T_{\alpha\beta}^{(pr)} E_{\beta}^{(r)} + \alpha^2 \sum_{rs} T_{\alpha\beta}^{(pr)} T_{\beta\gamma}^{(rs)} E_{\gamma}^{(s)} - \dots, \quad (7.8)$$

then eq. (7.7) reduces to

$$\Delta^2 = \frac{\alpha^2 \left\langle \sum_{pqrs} T_{\alpha\beta}^{(pr)} T_{\alpha\beta}^{(qs)} \right\rangle}{6N\gamma_R + 2\alpha^2 \left\langle \sum_{pqrs} (T_{\alpha\beta}^{(pr)} T_{\alpha\beta}^{(rs)} + T_{\alpha\beta}^{(qr)} T_{\alpha\beta}^{(rs)}) \right\rangle}. \quad (7.9)$$

This yields, by approximation,

$$\Delta^2 = \frac{\alpha^2 V}{6NkT\beta_T} \left\langle \sum_{qrs} T_{\alpha\beta}^{(pr)} T_{\alpha\beta}^{(qs)} \right\rangle = \frac{4\pi \alpha^2 V}{kT\beta_T} \int_0^{\infty} r^4 g(r) dr. \quad (7.10)$$

As  $F_{\text{anis}} \neq 0$ , the light scattered on assemblies of spherical molecules undergoes depolarisation ( $D \neq 0$ ). Buckingham and Stephen (1957) showed that, in the case under consideration, the degree of depolarisation  $D$  may be expressed by the difference between the molecular refraction of the fluid ( $R_M$ ) and that of the perfect gas ( $_{\text{gas}}R_M$ ).

*Polar liquids.* Buckingham and Stephen, in the theory proposed by them (1957), proved the value of the degree of depolarization  $D$  in polar liquids to be strongly dependent on the hyperpolarizability of the molecules.

If an isolated molecule possesses an axis of symmetry, and if this is the 3-axis, then the following components of the tensors  $\mu_i$ ,  $\alpha_{ij}$  and  $\beta_{ijk}$  have non-zero values:

$$\mu_3 \equiv \mu, \alpha_{11} = \alpha_{22} \equiv \alpha_1 \neq \alpha_{33} \equiv \alpha_3, \beta_{113} = \beta_{223} \equiv \beta_{13} \neq \beta_{333} \equiv \beta_{33}. \quad (7.11)$$

As a first approximation, expressions (7.1) and (7.2) may be reduced to the form

$$F_{\text{is}}(s) = \left\langle \sum_{pq} \{(\alpha_3 + 2\alpha_1) + (\beta_{33} + 2\beta_{13}) F_{03}\}^2 \frac{\sin sr_{pq}}{sr_{pq}} \right\rangle, \quad (7.12)$$

$$F_{\text{anis}}(s) = \frac{1}{2} \left\langle \sum_{pq} \{(\alpha_3 - \alpha_1) + (\beta_{33} - \beta_{13}) F_{03}\}^2 (3 \cos^2 \Theta(pq) - 1) \frac{\sin sr_{pq}}{sr_{pq}} \right\rangle. \quad (7.13)$$

Buckingham and Stephen (1957) showed that, in the case of Onsager's model (1936),

$$F_{03} = \frac{2(\varepsilon - 1)(n^2 - 1)}{3(2\varepsilon + n^2)} \cdot \frac{\mu}{\alpha}, \quad (7.14)$$

wherein  $\varepsilon$  is the static dielectric constant of the medium. Thus, for small scattering molecules, eqs. (7.12) and (7.13) reduce to

$$F_{is} = 9\alpha^2 \left\{ 1 + \frac{2(\varepsilon - 1)(n^2 - 1)}{3(2\varepsilon + n^2)} \frac{\mu\beta}{\alpha^2} \right\}^2 N\gamma_R, \quad (7.15)$$

$$F_{anis} = 9\alpha^2 \left\{ 1 + \frac{2(\varepsilon - 1)(n^2 - 1)}{3(2\varepsilon + n^2)} \frac{\mu\beta\delta_\beta}{\alpha^2\delta_\alpha} \right\}^2 \delta_\alpha^2 NR_{CM}, \quad (7.16)$$

$$\beta = \frac{1}{3}(\beta_{33} + 2\beta_{13}), \quad \delta_\beta = \frac{\beta_{33} - \beta_{13}}{3\beta}, \quad (7.17)$$

with  $\beta$  denoting the mean hyperpolarizability of the isolated dipolar molecule, and  $\delta_\beta$  yielding a measure of the anisotropy of its hyperpolarizability.

Substituting (7.15) and (7.16) with  $R_{CM} = 1$  in eq. (4.13), the Buckingham-Stephen formula for the degree of depolarization in polar liquids is obtained:

$$D = \frac{6 \left\{ 1 + \frac{4(\varepsilon - 1)(n^2 - 1)}{3(2\varepsilon + n^2)} \frac{\mu\beta\delta_\beta}{\alpha^2\delta_\alpha} \right\}^2 \delta_\alpha^2}{5 \left\{ 1 + \frac{4(\varepsilon - 1)(n^2 - 1)}{3(2\varepsilon + n^2)} \frac{\mu\beta}{\alpha^2} \right\}^2 \gamma_R + 7 \left\{ 1 + \frac{4(\varepsilon - 1)(n^2 - 1)}{3(2\varepsilon + n^2)} \frac{\mu\beta\delta_\beta}{\alpha^2\delta_\alpha} \right\}^2 \delta_\alpha^2}. \quad (7.18)$$

Similarly, by (5.5), the following formula for Rayleigh's ratio is obtained:

$$S = \frac{\pi^2 (n^2 - 1)^2 V}{2\lambda^4 N} \left\{ \left[ 1 + \frac{4(\varepsilon - 1)(n^2 - 1)}{3(2\varepsilon + n^2)} \frac{\mu\beta}{\alpha^2} \right] \gamma_R + \right. \\ \left. + \frac{13}{5} \left[ 1 + \frac{4(\varepsilon - 1)(n^2 - 1)}{3(2\varepsilon + n^2)} \frac{\mu\beta\delta_\beta}{\alpha^2\delta_\alpha} \right] \delta_\alpha^2 \right\}. \quad (7.19)$$

These are formulas which, if the quantities  $D$  and  $S$  are known from experimental data, yield the value of the hyperpolarizability of the isolated molecule.

### 8. General Relations

From the theory, as discussed in detail in §§ 3 to 7, it is seen that, in order to compute the quantities  $D$ ,  $S$  and  $h$  for a given condensed substance, the quantities accounting for the radial and angular intermolecular correlations should be known,

in addition to those describing the properties of the isolated molecules. Since, for a given substance, it may well be the case that not all the molecular parameters are known simultaneously, it is convenient to compute the quantities  $D$ ,  $S$  and  $h$  from relations containing only such quantities as are accessible to experimental determination.

*Relations between  $D$ ,  $S$  and  $h$ .* Eqs. (4.1) and (4.12) yield

$$\frac{F_{\text{anis}}(s)}{F_{\text{is}}(s)} = \Delta^2(\vartheta) = \frac{5 \{D(\vartheta) - \cos^2 \vartheta\}}{6 - 7D(\vartheta) + \cos^2 \vartheta}, \quad (8.1)$$

a relation whose left hand side coincides with the theoretical definition of the optical anisotropy of the medium, and whose right hand side makes it possible to compute  $\Delta^2$  directly from experimental data on the degree of depolarisation of the light scattered.

By (8.1), eq. (5.4) determining  $S(\vartheta)$  may be rewritten in the form

$$S(\vartheta) = \frac{1}{18V} \left( \frac{2\pi}{\lambda} \right)^4 \left( \frac{n^2 + 2}{3} \right)^2 \frac{\{6 + 6D(\vartheta)\} \sin^2 \vartheta}{6 - 7D(\vartheta) + \cos^2 \vartheta} F_{\text{is}}(s), \quad (8.2)$$

$$S(\vartheta) = \frac{1}{18V} \left( \frac{2\pi}{\lambda} \right)^4 \left( \frac{n^2 + 2}{3} \right)^2 \frac{\{6 + 6D(\vartheta)\} \sin^2 \vartheta}{5 \{D(\vartheta) - \cos^2 \vartheta\}} F_{\text{anis}}(s), \quad (8.3)$$

wherein  $F_{\text{is}}(s)$  and  $F_{\text{anis}}(s)$  are given by (2.22) and (2.23), and  $\vartheta$  is the angle of scattering.

If observation is perpendicular to the incident beam ( $\vartheta = 90^\circ$ ), eqs. (8.1) — (8.3) yield, for scattering molecules of small dimensions,

$$\frac{F_{\text{anis}}}{F_{\text{is}}} = \Delta^2 = \frac{5D}{6 - 7D}, \quad (8.4)$$

$$S = \frac{1}{18V} \left( \frac{2\pi}{\lambda} \right)^4 \left( \frac{n^2 + 2}{3} \right)^2 \frac{6 + 6D}{6 - 7D} F_{\text{is}}, \quad (8.5)$$

$$S = \frac{1}{18V} \left( \frac{2\pi}{\lambda} \right)^4 \left( \frac{n^2 + 2}{3} \right)^2 \frac{6 + 6D}{5D} F_{\text{anis}}. \quad (8.6)$$

Under identical conditions, by eq. (5.9) and with respect to (8.4), the extinction coefficient is obtained as follows:

$$h = \frac{8\pi}{27V} \left( \frac{2\pi}{\lambda} \right)^4 \left( \frac{n^2 + 2}{3} \right)^2 \frac{6 + 3D}{6 - 7D} F_{\text{is}}, \quad (8.7)$$

$$h = \frac{8\pi}{27V} \left( \frac{2\pi}{\lambda} \right)^4 \left( \frac{n^2 + 2}{3} \right)^2 \frac{6 + 3D}{5D} F_{\text{anis}}. \quad (8.8)$$



Finally, the foregoing expressions yield the general relations:

$$D(\vartheta) = D \left( 1 + \frac{1-D}{D} \cos^2 \vartheta \right), \quad (8.9)$$

$$S(\vartheta) = S \left( 1 + \frac{1-D}{1+D} \cos^2 \vartheta \right), \quad (8.10)$$

$$h = \frac{8\pi}{3} S \frac{2+D}{1+D}, \quad (8.11)$$

which hold for a medium of arbitrary density consisting of scattering molecules of small dimensions. Analogous relations were derived by Cabannes (1929) for light scattering on isolated molecules.

If the intermolecular field existing within the condensed medium be neglected, the molecular factor  $F_{\text{is}}$  of isotropic scattering may be expressed by experimentally known quantities. Namely, with respect to the Lorentz-Lorenz equation (5.14), eq. (3.10) yields

$$F_{\text{is}} = \frac{81}{16\pi^2} \left( \frac{n^2-1}{n^2+2} \right)^2 V kT \beta_T. \quad (8.12)$$

Substituting the foregoing expressions in eqs. (8.5) and (8.7), we obtain the Cabannes-King-Rocard formulas

$$S = \frac{\pi^2 (n^2-1)^2}{2\lambda^4} \frac{6+6D}{6-7D} kT \beta_T, \quad (8.13)$$

$$h = \frac{8\pi^3 (n^2-1)^2}{3\lambda^4} \frac{6+3D}{6-7D} kT \beta_T,$$

which contain no molecular parameters and may be checked experimentally.

*Anisotropic light scattering and Kerr effect.* The molecular factor  $F_{\text{anis}}$  accounting for anisotropic scattering may be expressed by the anisotropic term in Kerr's constant. By a general relation,

$$F_{\text{anis}} = \frac{1215 n^2 (n^2-1) kTV}{2\pi (\epsilon-1) (\epsilon+2) (n^2+2)^3} K_{\text{anis}}, \quad (8.14)$$

wherein  $\epsilon$  denotes the electric permittivity of the medium. The anisotropic term in Kerr's constant is, in general, given by the following expression (cf. Kielich 1958b):

$$K_{\text{anis}} = \frac{\pi (n^2+2)^2 (\epsilon+2)^2}{1215 n^2 kTV} \left\langle (3\delta_{\sigma\nu} \delta_{\tau\varrho} - \delta_{\sigma\tau} \delta_{\nu\varrho}) \sum_{pq} \frac{\partial m_{\sigma}^{(p)}}{\partial E_{\tau}} \frac{\partial m_{\nu}^{(q)}}{\partial E_{\varrho}} \right\rangle \quad (8.15)$$

with  $m_{\sigma}^{(p)}$  denoting the dipole moment induced in the molecule by the variable electric field  $\mathbf{E}$  of the light wave, and  $m_{\nu}^{(q)}$  — the total dipole moment of the  $q$ -th molecule in the presence of the static electric field  $\mathbf{E}_0$  inducing optical birefringence in the medium.

For molecules possessing constant polarizability, eq. (8.15) yields

$$K_{\text{anis}} = \frac{\pi(n^2 + 2)^2 (\varepsilon + 2)^2 \alpha_{ij} a_{kl}}{1215 n^2 kTV} \left\langle \sum_{pq} (3\omega_{ik}^{(pq)} \omega_{jl}^{(pq)} - \delta_{ij} \delta_{kl}) \right\rangle \quad (8.16)$$

wherein  $a_{ij}$  is the electric polarizability tensor of the isolated molecule. In particular, if the molecules have the axial symmetry, eq. (8.16) reduces to

$$K_{\text{anis}} = \frac{(n^2 - 1) (\varepsilon - 1) (n^2 + 2) (\varepsilon + 2) V}{120\pi n^2 kTN} \delta_a \delta_a R_{CM}, \quad (8.17)$$

with  $R_{CM}$  denoting the correlation factor given by (3.22).

For the case of a condensed medium consisting of spherical molecules, the general expression (8.15) yields

$$K_{\text{anis}} = \frac{\pi (n^2 + 2)^2 (\varepsilon + 2)^2 \alpha a}{1215 n^2 kTV} \left\langle \sum_{pq} \left( 3 \frac{\partial F_a^{(p)}}{\partial E_\beta} \frac{\partial F_a^{(q)}}{\partial E_{o\beta}} - \frac{\partial F_a^{(p)}}{\partial E_a} \frac{\partial F_\beta^{(q)}}{\partial E_{o\beta}} \right) \right\rangle, \quad (8.18)$$

or, as a first approximation:

$$K_{\text{anis}} = \frac{\pi (n^2 + 2)^2 (\varepsilon + 2)^2 \alpha^2 a^2}{405 n^2 kTV} \left\langle \sum_{pqrs} T_{\alpha\beta}^{(pr)} T_{\alpha\beta}^{(qs)} \right\rangle. \quad (8.19)$$

The quantities  $D$ ,  $S$ ,  $h$ , and Kerr's constant  $K_{\text{anis}}$ . Substituting eq. (8.14) in (8.6) and (8.8), we obtain the general expressions

$$S = \frac{72\pi^3 n^2 (n^2 - 1) kT}{\lambda^4 (\varepsilon - 1) (\varepsilon + 2) (n^2 + 2)} (1 + D^{-1}) K_{\text{anis}}, \quad (8.20)$$

$$h = \frac{192\pi^4 n^2 (n^2 - 1) kT}{\lambda^4 (\varepsilon - 1) (\varepsilon + 2) (n^2 + 2)} (1 + 2D^{-1}) K_{\text{anis}}, \quad (8.21)$$

which contain experimentally accessible quantities only, and hold for condensed media consisting of molecules of arbitrary symmetry.

Combining expression (8.4) and eqs. (8.12) and (8.14), we have

$$\frac{5D}{6 - 7D} = \frac{120\pi n^2}{(n^2 - 1) (\varepsilon - 1) (n^2 + 2) (\varepsilon + 2)} \frac{K_{\text{anis}}}{\beta_T}; \quad (8.22)$$

hence, Gans' formula (1923) is obtained:

$$K_{\text{anis}} = \frac{(n^2 - 1) (\varepsilon - 1) (n^2 + 2) (\varepsilon + 2)}{24\pi n^2} \cdot \frac{\beta_T D}{6 - 7D}, \quad (8.23)$$

which yields a relation between Kerr's constant and the degree of depolarisation of the light scattered.

Substituting  $F_{is}$  and  $F_{anis}$  as given by (8.12) and (8.14) in eqs. (5.5) and (5.9), we have

$$S = \frac{\pi^2 (n^2 - 1)^2}{2\lambda^4} kT \left\{ \beta_T + \frac{312\pi n^2 K_{anis}}{(n^2 - 1)(\epsilon - 1)(n^2 + 2)(\epsilon + 2)} \right\}, \quad (8.24)$$

$$h = \frac{8\pi^3 (n^2 - 1)^2}{3\lambda^4} kT \left\{ \beta_T + \frac{240\pi n^2 K_{anis}}{(n^2 - 1)(\epsilon - 1)(n^2 + 2)(\epsilon + 2)} \right\}. \quad (8.25)$$

**Conclusions.** The quantities  $D$ ,  $S$  and  $h$  accounting for light scattering in an isotropic medium are given (§§ 4–7) in terms of various molecular parameters inaccessible to experiment; on the other hand, the same quantities are related mutually and with Kerr's constant, thus yielding the basis for comparing the theoretically predicted results and those obtained experimentally. Thus, a study of light scattering may serve not only to determine the shape and properties of the isolated molecules, but also to obtain valuable data on the nature of the molecular interaction existing in a condensed medium.

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## ZUR FESTSTELLUNGSMÖGLICHKEIT EINER PLASTISCHEN DEFORMATION MIT HILFE EINES GEIGER-SPITZENZÄHLERS

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Es wird der Einfluss einer inneren Deformation auf die photostimulierte Koexoelektronenemission von Aluminium-Proben untersucht. Die innere, durch Einpressung von Stahlstäben erreichte Deformation lässt sich wegen der langsameren Abklingung der Emissionsintensität in der Druckpunktumgebung feststellen. Es werden zwei Deutungsmöglichkeiten diskutiert: Eine durch Herstellung von Emissionszentren, die aus dem Innern der deformierten Probe nach der Oberfläche diffundieren, die zweite durch eine mit der Deformation verbundenen Kohäsionsänderung der Oberflächenschicht. Im weiteren werden Messergebnisse über die Feststellungsmöglichkeit von Druckeingriffen in Polymer-Proben bei Ausnützung des Einflusses der bei Druckeingriffen entstehenden Elektrisierungszuständen auf die Arbeitsbedingungen des Zählers, angeführt.

Kramer (1950) hat auf das Ansprechen eines offenen Geiger-Spitzenzählers auf sogenannte „Exoelektronen“ (Bericht über die Diskussionstagung, 1957) hingewiesen, welche von deformierten Oberflächen einiger Metalle während oder nach der Deformation emittiert werden. Einige Jahre später wurde von einem der Verfasser (Sujak 1957 a, b) gezeigt, dass der Geiger-Zähler auch zu Untersuchungen von deformierten Polymer-Oberflächen sich eigne indem der Einfluss der im Deformationsbereich entstehenden Elektrisierung auf die Arbeitsbedingungen des Zählers ausgenutzt wird.

In der vorgelegten Arbeit werden weitere, das erwähnte Problem betreffende Ergebnisse angeführt. Das erste Ergebnis betrifft den Einfluss einer sogenannten inneren Deformation von Aluminium auf die photostimulierte Koexoelektronenemission, das zweite eine Erzeugung von elektrisierten Gebieten beim Deformieren von Plexiglas. In beiden Fällen erlaubt die durch den Geiger-Zähler in der Zeiteinheit registrierte Impulszahl eine Feststellung wie auch relatives Vergleichen von den vorher plastisch deformierten Bereichen. Die angeführten Ergebnisse sollen einen weiteren Beitrag zur Ausarbeitung einer neuen Untersuchungsmethode von plastischen Deformationen in Metallen und in aus organischen Stoffen hergestellten, für das weisse Licht undurchsichtigen Elementen bilden.

*Einfluss einer inneren Deformation auf die photostimulierte Koexoelektronenemission aus der Oberfläche des technischen Aluminiums*

Die photostimulierte Exoelektronenemission aus Metalloberflächen nach vorangehender, im weitesten Sinne des Wortes gemeinten Bearbeitung (mechanische Abschabung, plastische Deformation, Beleuchtung mit elektromagnetischer und korpuskulärer Strahlung, Temperung usw.) erregt Interesse wegen hervortretenden Erklärungsmöglichkeiten einiger, die Festkörper-Oberfläche betreffender Probleme, wie auch wegen Aussichten auf technische Anwendung. Das angehäuften experimentellen Material erlaubt einstweilen keine eindeutige Klärung des Emissionsmechanismus, obwohl er in groben Umrissen verständlich zu sein scheint.

Die Exoelektronenemission wird heutzutage mit den durch Elektronen besetzten Kristallgitter-Defekten einer vorangehend auf der Metalloberfläche erzeugten Oxydschicht gebunden. Wenn die erwähnten Kristallgitter-Defekte der Oxydschicht, die wie Haftstellen wirken, während einer Bearbeitung entstehen, können sie dann — wenn sie sich gleichzeitig mit Elektronen füllen — später als Elektronenquellen dienen (Sujak 1959). Eine zweite Auffassung sieht den Mechanismus der photostimulierten Exoelektronenemission aus mechanisch bearbeiteten Metalloberflächen als Begleiterscheinung einer chemischen Reaktion (z. B. Oxydation) zwischen der frisch abgedeckten Metalloberfläche und der mit dieser kontaktierenden Gasatmosphäre (Sujak 1959). In welchem Grade beide oben erwähnte Mechanismen miteinander verbunden sind, ist vom heutigen Standpunkt aus schwer zu beurteilen. Im Allgemeinen wird jedoch angenommen, dass die Oberflächendeformation, die entweder zur Erzeugung von Kristallgitter-Defekten in der Oxydschicht und deren Elektronenfüllung, oder zur Freilegung frischer Metalloberflächen durch Zerreißen der Oxydschicht führt, die Hauptrolle spielt. Im ersten wie im zweiten Falle kann also als Resultat einer Deformation dünner Oberflächenschichten die photostimulierte Exoelektronenemission einsetzen, wenn jedoch eine für das gegebene Material entsprechende elektromagnetische Strahlung (Licht) zur Stimulierung benutzt wird. Die Oberflächendeformation von Aluminium wurde bisher durch Kratzen, Schaben oder Dehnen hervorgerufen (Grunberg und Wright 1957).

In unserem Falle wurden die Aluminium-Proben sowohl oberflächlich wie auch innerlich deformiert. Die Oberflächendeformation beruhte auf einer mit Stahl durchgeführten Abschabung der Deckschicht, die innere auf einem Eindringen eines Stahlstabes in die Probe. Wie sich zeigte, hat die Deformation des Innern grossen Einfluss auf die Intensität der photostimulierten Exoelektronenemission. Infolge verschiedener Abklingungsgeschwindigkeiten der Emission konnten die einer plastischen Deformation des Innern unterzogenen Gebiete lokalisiert werden. Es wurde eine Reihe von Versuchen an Proben aus technischem Aluminium durchgeführt, die — aus einem Flachstück geschnitten — das Ausmass  $60 \times 30 \times 8$  mm besaßen. Die Proben wurden bei ständig kontrollierter photostimulierter Koexoelektronenemission der Reihe nach einer oberflächlichen, einer inneren und wieder einer oberflächlichen Deformation unterzogen.

## a) Die Oberflächendeformation

Nach Durchführung der Oberflächendeformation, die auf einer Abschabung mit Feile und Stahldrahtbürste einer ungefähr 0,5 mm starken Schicht beruhte, wurde die Probe auf einen verschiebbaren Tisch unter den offenen Geiger-Spitzenzähler gebracht (Fig. 1). Der Abstand Probenoberfläche-Zähler wurde beim Verschieben der Probe konstant eingehalten und betrug etwa 4 mm. Eine 6V-35 W-Wolfram-Lampe

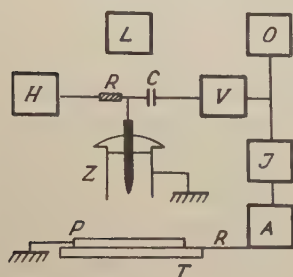


Fig. 1

Fig. 1. Schematische Darstellung der Versuchsanordnung: H — Hochspannungsspeisegerät, V — Impulsverstärker, I — Impulsintegrator, A — Schreibender Amperemeter, O — Oszilloskop, Z — Geiger-Spitzenzähler, L — Lichtquelle, P — Probe, T — Tisch, R — Papier-Registrierband

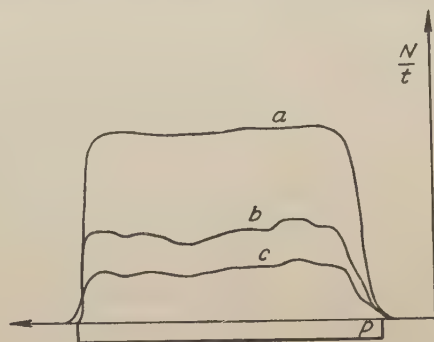


Fig. 2

Fig. 2. Der Verlauf der photostimulierten Koexoelektronenemission von einer abgeschabten Aluminium-Probe. Kurve *a* unmittelbar nach der Bearbeitung gemessen, Kurven *b* und *c* entsprechend 7 und 14 Minuten später.

beleuchtete durch eine Glaslinse und eine gleichzeitig als Zählerspitzenbefestigung dienende Plexiglaslinse die untersuchte Oberfläche. Die durch die photostimulierte Exoelektronenemission hervorgerufenen Zählerimpulse wurden nach Verstärkung durch ein Integrator mittels eines schreibenden Amperometers registriert. Die Registrierrolle des Amperometers war mit dem verschiebbaren Tisch gekoppelt. Wie aus Fig. 2 zu ersehen ist, ist die der untersuchten Probe entlang gemessene Intensität der photostimulierten Koexoelektronenemission nach den oben angeführten Eingriffen fast konstant. Die Emissionsintensität ist in willkürlichen Einheiten ausgedrückt. Die zeitliche Abklingung der Emission verläuft auch fast gleichmässig für alle Oberflächenbereiche der Probe. Kurve *a* entspricht einer Messung unmittelbar nach der Bearbeitung, Kurven *b* und *c* — 7 und 14 Minuten später. Während der Messung wurden immer nur die jeweilig abgetasteten Flächenelemente beleuchtet. Die Emissionsintensität ohne gleichzeitiger Photostimulation konnte nicht ausgemessen werden, da sie in den Grenzen der Dunkelstosszahl des Zählers lag.

## b) Die innere Deformation

In der zweiten Bearbeitungsphase wurde in eine der Seitenflächen der Probe ein Stahlstab eingedrückt (Fig. 3). Um die parallel zu dieser laufenden Seitenfläche vor unregelmässigem Druck zu schützen, wurde die Probe vorher auf eine plane

Holzunterlage gelegt. Nach Durchführung der Stabeinpressung (es wurden Stahlstäbe mit verschiedenen Profilen angewendet) wurde die Probe mit Feile und Bürste geebnet. Die gleich darauffolgende Messung des Intensitätsverlaufes der photostimulierten Koexoelektronenemission wurde entlang der in Fig. 3 eingezeichneten Linie  $a$  durchgeführt, die ungefähr 8 mm vom Boden der Druckkerbe entfernt war. Kurven der photostimulierten Koexoelektronenemission zeigten bei festgelegten geometrischen Bedingungen verschiedene, von der nach Stabeinpressung verfloßenen Zeit

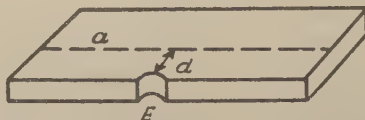


Fig. 3. Aluminium-Probe mit Druckkerbe. E — Einpressstelle,  $a$  — Messlinie

abhängende Verläufe (Fig. 4). Kurve  $a$  entspricht einer Messung gleich nach der Ebnung mit Feile und Bürste (Oberflächendeformation). Nach 24-stündiger Lagerung ohne Lichtzutritt wurde Kurve  $b$  aufgenommen. Wie man sieht, prägt sich ein deutliches Maximum ( $W$  in Fig. 4) aus. Die zeitliche Gestaltung eines solchen Maximums zeigt Fig. 5.

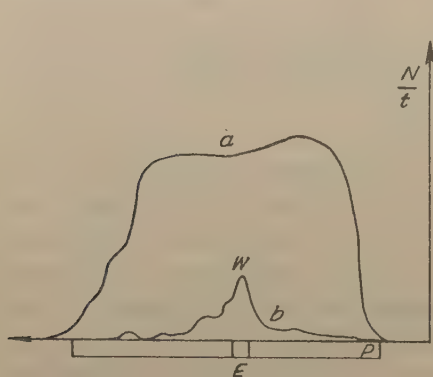


Fig. 4

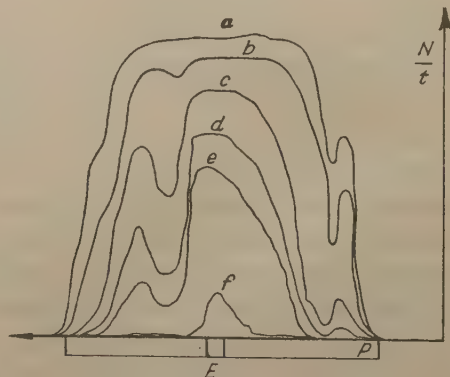


Fig. 5

Fig. 4. Der Verlauf der photostimulierten Koexoelektronenemission von einer oberflächlich und innerlich bearbeiteten Aluminium-Probe. P — Probe, E — Einpressstelle, Kurve  $a$  unmittelbar nach der Bearbeitung gemessen, Kurve  $b$  24 Stunden später.

Fig. 5. Maximum-Ausprägung im Druckbereich einer oberflächlich und innerlich bearbeiteten Aluminium-Probe. P — Probe, E — Einpressstelle, Kurve  $a$  unmittelbar nach der Bearbeitung, Kurven  $b$  bis  $f$  entsprechend 6, 15, 21, 27 und 60 Minuten später gemessen.

An einer frisch in obiger Weise bearbeiteten Probe wurde in verschiedenen Zeitpunkten der Intensitätsverlauf entlang der Linie  $a$  (Fig. 3) gemessen. Kurve  $a$  entspricht einer Messung unmittelbar nach der Bearbeitung, die Kurven  $b$  bis  $f$  entsprechend 6, 15, 21, 27 und 60 Minuten später. Wie schon vorher erwähnt, wurde



die Probe nur während der Messung beleuchtet. Wie man sieht, tritt mit der Zeit eine deutliche Selektivität der Emissionsintensitäts-Verteilung in der Umgebung der Einpressstelle (innere Deformation) ein. Die Emissionsintensität klingt also langsamer in unmittelbarer Umgebung der Einpressstelle als in übrigen Oberflächengebieten der Probe ab. Wenn als Messlinien parallel zu  $a$  (Fig. 3) laufende Linien gewählt werden, kann der Wirkungsbereich der inneren Deformation in Abhängigkeit vom Profil der eingepressten Stäbe ermittelt werden. Die Aussetzung der innerlich und oberflächlich deformierten Probe auf längere Lichteinwirkung (z. B. Tageslicht) bewirkt ein fast vollständiges Herabsinken des Emissionsvermögens. Nach wiederholter Abschabung der dünnen (ungefähr 0.3 mm) Oberflächenschicht einer solchen Probe wurde keine Entwicklung einer selektiven Intensitätsverteilung der Emission mehr in der Umgebung der Einpressstelle festgestellt.

Die durch Knicken und darauffolgendes Gerademachen sowie durch seitliche Einpressung von Stahlspitzen erreichte innere Deformationen führten zu ähnlichen Ergebnissen. Der sichtliche Einfluss der inneren Deformation auf die Exoelektronenemission von oberflächlich bearbeitetem Aluminium kann auf zweierlei Weise gedeutet werden. Erstens als Herstellung im deformierten (Metall!) Volumen gewisser, nach der Oberfläche diffundierenden Zentren, die danach selbst als Exoelektronenquellen auftreten oder durch lokale Energieabgabe auf die Exoelektronenemission aus anderen Zentrenarten einwirken. Für diesen Mechanismus würde die Tatsache sprechen, dass sich das Emissionsmaximum in der Umgebung der inneren Deformation unabhängig (in erster Näherung) von der Stärke der nach Deformationsvollführung abgeschabten Oberflächenschicht ausprägt, sowie auch das Ausbleiben des Maximums nach völliger „Bleichung“ durch Lichteinstrahlung und darauffolgender Oberflächenbearbeitung.

Der zweite mögliche Mechanismus einer Ausprägung des angeführten Maximums würde auf einer durch die innere Deformation hervorgerufenen Kohäsionsänderung der Oberflächenschicht beruhen. Diese Kohäsionsänderung könnte sich in einer mikroporösen Oberflächenstruktur der Deformationspunktumgebung, also in Herstellung von effektiv grösserer „frischer Oberfläche“ auswirken (siehe auch Gobrecht 1954). Der erschwerte Transport von Sauerstoffmolekülen in einer und Photoelektronen (Sauerstoffionen) in entgegengesetzten Richtung würde die langsamere Oxydation der mikroporösen Oberfläche im Vergleich mit der übrigen Probenoberfläche beeinflussen. Dieses würde das langsamere Abklingen der Prädisposition zur photostimulierten Koexoelektronenemission aus der Umgebung der Einpressstelle begründen, da die übrige Probenoberfläche nur einer seichten Oberflächenbearbeitung unterzogen wurde. Für diesen Mechanismus sprechen die Tatsachen, dass die Exoelektronenemission nicht im Hochvakuum auftritt (Lohff und Raether 1955, Lohff 1956), wie auch das Verschwinden der Emissionsfähigkeit von oberflächlich bearbeiteten Aluminium-Proben nach Einwirkung einer Hochfrequenzentladung in Luftatmosphäre (Sujak und Mader 1958). Die Entscheidung, welcher von diesen Mechanismen die Hauptrolle spielt, wie auch der Mittwirkungsgrad beider ist fortgehend Gegenstand weiterer Untersuchungen.

# *Einfluss der Deformation von Polymeren auf die Dunkelstosszahl des Zählers*

Die Feststellung einer plastischen Deformation in Aluminium mit dem Geiger-Zähler beruht auf Intensitätsmessungen der Koexoelektronenemission. Bei Polymeren wurde jedoch bisher keine während oder nach einer plastischen Deformation einsetzende Exoelektronenemission festgestellt. Es kann sein, dass eine photostimulierte Exoelektronenemission aus einer deformierten Polymer-Probe erst nach entsprechend energetischer Ultravioletteinstrahlung einsetzen würde, die Einstrahlung von Wellenlängen unter  $2000 \text{ \AA}$  während der Zählermessungen ruft jedoch eine Photoelektronenemission aus der Zählerkathode hervor, was die Feststellung einer eventuellen Exoelektronenemission aus der Probenoberfläche gänzlich unmöglich macht. Um also die Deformation einer Polymer-Probe mit dem Spitzenzähler festzustellen und auszumessen muss eine andere Erscheinung als die Exoelektronenemission ausgenutzt werden. Während der Deformation durch Eindringen entstehen Kontakt-Elektrisierungen (Triboelektrizität) sowie auch elektrische Polarisierungserscheinungen, die dann mit dem Zähler abgetastet werden können (vergleiche auch z. B. Bazan 1959).

Die auf solche Weise elektrisierten Gebiete einer deformierten Polymer-Probe können dank der Eindringung ihrer elektrostatischen Felder in das Innere des Zählers

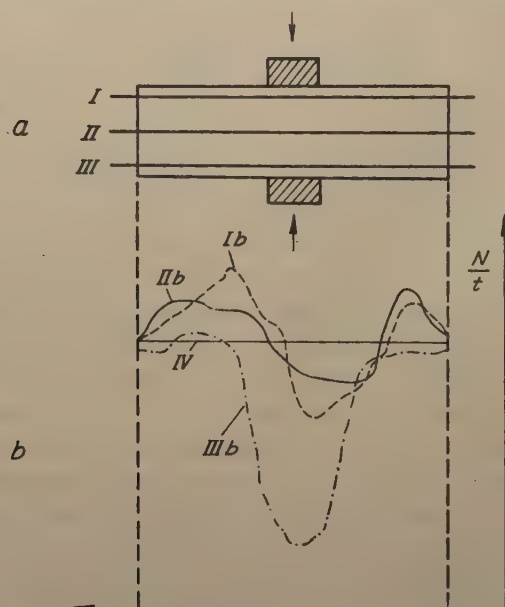


Fig. 6. Elektrisierungsverteilung einer Plexiglasplatte nach der Druckdeformation. a) Messprobe mit eingezeichneten Messlinien I, II und III. Die Pfeile geben die Druckpunkte an. b) Kurven Ib, IIb und IIIb entsprechen der Dunkelstosszahl-Änderung des mit einer dielektrischen Kappe geschlossenen Zählers, entlang der Messlinien I, II und III gemessen. Kurve IV — Kontrollmessung vor der Druckdeformation.

qualitativ festgestellt und verglichen werden. Dieses Problem war schon Gegenstand früherer Veröffentlichungen (Sujak 1957a, b; Lewowski und Sujak 1959). Dort wurde das Arbeitsprinzip wie auch eine Reihe von wesentlichen Versuchsergebnissen über die relative Messung von Verteilungen der Elektrizitätszustände auf Oberflächen deformierter Isolatoren angegeben. Der Geiger-Zähler musste, um das Ionenerzeugende Gebiet (Zählvolumen des Zählers) von der untersuchten Oberfläche zu trennen mit einer dielektrischen Kappe abgeschlossen werden. Die Versuchsanordnung war der in Fig. 1 dargestellten ähnlich. Als Beispiel wird die Elektrisierungsverteilung einer Plexiglasplatte ( $62 \times 18 \times 6$  mm), die vorangehend einer schematisch in Fig. 6a gezeigten Druckdeformation unterzogen wurde, angeführt. Die deformierte Plexiglasplatte wurde unter dem Geiger-Spitzenzähler (Abstand Probenoberfläche-Zähler etwa 2 mm) entlang der Linien I, II und III (Fig. 6a) verschoben. Der Zähler reagierte auf die lokale Elektrisierungszustände mit einer Änderung seiner Dunkelstosszahl wie es Kurven Ib, IIb und IIIb in Fig. 6b zeigen. Die Kurven wurden — wie im ersten Teil — durch ein schreibendes Amperemeter auf einem Papier-Registrierband aufgetragen.

Die Untersuchungen von Polymer-Deformationen mit dem Geiger-Spitzenzähler scheinen besonders Vorteilhaft im Falle einer optischen Undurchsichtigkeit des Materials der untersuchten Probe zu sein.

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## SPIN-WAVE RESONANCES IN ANTIFERROMAGNETICS

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The purpose of this paper is to ascertain, whether a spin wave resonance effect in antiferromagnetics analogous to that predicted by C. Kittel (Phys. Rev., **110**, 1295 (1958)) for ferromagnetics is possible. By means of semiclassical formalism, the author shows the possibility of exciting odd modes of spin waves in antiferromagnetics and calculates the resonance values of applied magnetic field for these modes. Each mode can be excited by two different values of applied field. The investigated phenomenon might be probably observable in films 3—10 times thicker than in the case of ferromagnetics.

*Introduction*

Some months ago Kittel (1958) has predicted the possibility of exciting exchange modes of standing spin-waves in a thin ferromagnetic plate by a uniform radio-frequency field. He has proposed the term "spin-wave resonance" for this effect. The basic assumption which leads to the exciting of spin-wave modes is the spin pinning boundary condition, proposed by Kittel. Here the spins are assumed to be pinned down at the surface of the specimen, owing to the magnetic anisotropy energy which must be much greater at the surface than in the interior. Consequently, the spin waves can be considered practically as the sinusoidal standing waves with nodes at the boundaries. It follows, that only odd modes of spin waves are allowed.

The effect of ferromagnetic spin-wave resonances has been observed by Seavey and Tannenwald (1958) for permalloy film of 5600 Å thickness. The results agree in principle with Kittel's predictions.

In the present paper we attempt to investigate the analogous effect in antiferromagnetics. We use the approach similar to that of Kittel, although with some modifications. We apply indeed the semiclassical theory of spin waves, nevertheless we consider the discretely localised spins. Moreover, instead of linearly polarized radio-frequency field we take into account only one of his two circularly polarized compo-

nents, namely the one which rotates in the sense of spin precession. Such approach is suggested by the paper of Bloch and Siegert (1940), who have shown, that the other circularly polarized component causes only an inobservably small displacement of resonance frequency. We get two advantages from such an approach. First, the semi-classical equation of spin motion is strictly satisfied by wave-precessional solution (otherwise, the equation for  $S^z$  is satisfied only approximately). And second, the iteration made by Kittel is not necessary in that case. This iteration of simultaneous differential equations for  $S^z$  and  $S^y$  leads to two series of spin-wave resonances for each  $\omega$  ( $\omega = \pm \omega_p$  in the notation of Kittel), one of which must be fictitious.

### Derivation of the resonance formula

Let us consider an antiferromagnetic plate with parallel plane faces. Taking  $\mathbf{j}_x, \mathbf{j}_y, \mathbf{j}_z$  as unit vectors of cartesian coordinate system, we choose  $\mathbf{j}_x$  and  $\mathbf{j}_y$  parallel to the plate surface. As mentioned above, from the radiofrequency field

$$2H_R e^{i\omega t} \mathbf{j}_x = H_R e^{i\omega t} (\mathbf{j}_x + i\mathbf{j}_y) + H_R e^{i\omega t} (\mathbf{j}_x - i\mathbf{j}_y) \quad (1)$$

we retain the first term only (therefore our  $H_R$  corresponds to Kittel's  $H_1/2$ ). Furthermore we take both the anisotropy field  $\mathbf{H}_A$  and the applied field  $\mathbf{H}$  in the direction of  $z$ -axis.

In analogy to Kittel's quoted paper we consider only a chain of  $N$  spins with spacing  $a$  aligned along the  $z$ -axis. Then, the equation of motion of  $m$ -th spin is:

$$\begin{aligned} \dot{\mathbf{S}}_m &= \mathbf{S}_m \times (2J/\hbar) (\mathbf{S}_{m-1} + \mathbf{S}_{m+1}) + \\ &+ \mathbf{S}_m \times \gamma [(H^z + (H_A)^z_m) \mathbf{j}_z + H_R e^{i\omega t} (\mathbf{j}_x + i\mathbf{j}_y)] \end{aligned} \quad (2)$$

$J$  being the exchange integral between nearest neighbours, the coefficient  $\gamma < 0$  — the magnetomechanical ratio and  $\hbar$  — the Planck's constant divided by  $2\pi$ . We take the solution of (2) in the form:

$$\mathbf{S}_m = e^{i\omega t} (\mathbf{j}_x + i\mathbf{j}_y) \sum_p R_p^{(m)} \sin ak_p m + S_m^z \mathbf{j}_z \quad (3)$$

where  $k_p = p\pi/aN$ . Substituting (3) into (2) and taking

$$S_m^z = S, \quad (H_A)^z_m = -H_A, \quad R_p^{(m)} = R_p^I$$

for the first sublattice and

$$S_m^z = -S, \quad (H_A)^z_m = H_A, \quad R_p^{(m)} = R_p^{II}$$

for the second one and moreover writing  $H^z = -H$ , we get:

$$\left. \begin{aligned} \sum_p b_p \sin ak_p m &= -\gamma H_R \\ \sum_p c_p \sin ak_p m &= -\gamma H_R \end{aligned} \right\} \quad (4)$$

where

$$\begin{aligned} b_p &= R_p^I [\omega + \gamma(H + H_A) + \eta] + R_p^{II} \eta \cos ak_p \\ c_p &= R_p^I \eta \cos ak_p - R_p^{II} [\omega + \gamma(H - H_A) + \eta] \\ \eta &= 4SJ/\hbar \end{aligned}$$

We see that the coefficients of sines must be correspondingly equal:

$$b_p = c_p$$

which leads to

$$b_p = R_p^I \frac{Q_p}{M_p^I} = R_p^{II} \frac{Q_p}{M_p^{II}} \quad (5)$$

where

$$\begin{aligned} Q_p &= (\gamma H - \omega)^2 + \gamma^2 H_A^2 - \eta [2\gamma H_A + \eta \cos ak_p (2 - \cos ak_p)] \\ M_p^I &= \omega + \gamma H - \gamma H_A - \eta \cos ak_p \\ M_p^{II} &= -\omega - \gamma H - \gamma H_A - \eta \cos ak_p \end{aligned}$$

We shall calculate the coefficients  $b_p$  multiplying both sides of (4) by  $\sin(q\pi m/N)$  and summing from  $m = 1$  to  $m = N$ .

Using the relations (see Appendix):

$$\sum_{m=1}^N \sin(p\pi m/N) \sin(q\pi m/N) = \frac{N}{2} \delta_{pq} \quad (6)$$

$$\sum_{m=1}^N \sin(q\pi m/N) = \begin{cases} 0 & \text{for } q \text{ even} \\ 2N/\pi q & \text{for } q \text{ odd} \end{cases} \quad (7)$$

we obtain

$$b_p = \begin{cases} 0 & \text{for } p \text{ even} \\ -4S\gamma H_R/\pi p & \text{for } p \text{ odd} \end{cases}$$

and therefore:

$$\begin{aligned} R_p^I &= -\frac{4S\gamma H_R}{\pi p} \cdot \frac{M_p^I}{Q_p} \\ R_p^{II} &= -\frac{4S\gamma H_R}{\pi p} \cdot \frac{M_p^{II}}{Q_p} \end{aligned} \quad (8)$$

### Discussion

As can be seen, for the amplitudes (8) the resonance occurs for  $Q_p = 0$  (provided, that  $M_p^I$  or  $M_p^{II}$  respectively do not vanishes simultaneously). From this condition we get the resonance values  $H_p$  of applied field for a given frequency:

$$H_p = -\frac{\omega}{\gamma} \pm \sqrt{(H_A + H_E)^2 - H_E^2 \cos^2 ak} \quad (9)$$

where

$$H_E = \eta/\gamma > 0$$

For small  $p$  we can take:  $\cos^2 ak \approx 1 - a^2 k^2$   
and therefore

$$H_p = H_\omega \pm \sqrt{H_A(H_A + 2H_E) + Cp^2} \quad (10)$$

where

$$C = H_E^2 \pi^2 / N^2 \quad \text{and} \quad H_\omega = -\omega/\gamma > 0$$

For each  $p$  there occur two resonance values of applied field. For  $p = 0$  we get the well-known formula for the main resonance.

Let us introduce the abbreviation:  $H_A(H_A + 2H_E) = B$ . Then, the interval between two successive odd-mode peaks is

$$\begin{aligned} \Delta H_{\text{ant}} = |H_{p+2} - H_p| &= \frac{4C(p+1)}{\sqrt{B + C(p+2)^2} + \sqrt{B + Cp^2}} \\ &\approx \frac{4C(p+1)}{2\sqrt{B + Cp^2}} \end{aligned}$$

The effects of anisotropy fields are usually small:  $H_A \sim 10^{-2} H_E$ . Taking  $N \sim 10^3$  and  $p < 20$  as in experiments of Seavey and Tannenwald, we have approximately  $B + Cp^2 \approx 2H_A H_E$ . Consequently we get:

$$\Delta H_{\text{ant}} \approx \frac{2H_E^2 \pi^2}{N^2 \sqrt{2H_A H_E}} (p+1)$$

Comparing this with the value of corresponding interval for the ferromagnetic case:

$$\Delta H_{\text{fer}} = 2H_E' \frac{\pi^2}{N^2} (p+1)$$

where  $H_E' = 4JS/|\gamma|\hbar$  ( $J < 0$ ), we see that for the same  $|J|$ ,  $S$ ,  $a$  and  $N$  values the ferromagnetic resonance peaks lie  $\sqrt{H_E/2H_A}$  times nearer than in our case. Hence, the antiferromagnetic observations can be made using 3—10 times thicker films than in experiments for ferromagnetics (provided that the absolute value of exchange integral has the same order of magnitude in both cases).

It seems, that actually the most suitable antiferromagnetic substance for such experiments should be chromium.

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## Appendix

One can verify the equality (9) as follows:

$$s = \sum_{m=1}^N \sin \frac{p\pi m}{N} \sin \frac{q\pi m}{N} = \frac{1}{4} \sum_{m=1}^N \left\{ -\exp \frac{i(p-q)\pi m}{N} - \exp \frac{-i(p-q)\pi m}{N} + \exp \frac{i(p+q)\pi m}{N} + \exp \frac{-i(p+q)\pi m}{N} \right\}$$

Each of four sums is a finite geometrical series, so that

$$4s = \frac{\exp [i\pi(p-q)] - 1}{1 - \exp [-i\pi(p-q)/N]} + \frac{\exp [-i\pi(p-q)] - 1}{1 - \exp [i\pi(p-q)/N]} - \frac{\exp [i\pi(p+q)] - 1}{1 - \exp [-i\pi(p+q)/N]} - \frac{\exp [-i\pi(p+q)] - 1}{1 - \exp [i\pi(p+q)/N]}$$

For  $p \rightarrow q$  both the first and the second term tend to  $N$  and the other two terms tend to zero. For each  $p \neq q$  however we have

$$e^{i\pi(p-q)} = e^{-i\pi(p-q)} = e^{i\pi(p+q)} = e^{-i\pi(p+q)} = \pm 1$$

For the upper sign we have  $s = 0$ ; for the lower one the considered sum  $s$  also vanishes because of the identity

$$\frac{1}{1 - e^{\alpha}} + \frac{1}{1 - e^{-\alpha}} \equiv 1$$

Therefore, the relation (9) is verified.

We can treat the sum (10) approximately because always  $N \gg p \gg 1$  for the spin wave resonances phenomena. We have then

$$\sum_{m=1}^N \sin(p\pi m/N) = \frac{\sin \frac{p\pi}{2} \cdot \sin \frac{p\pi(N+1)}{2N}}{\sin \frac{p\pi}{2N}} \approx \frac{\sin^2 \frac{p\pi}{2}}{\frac{p\pi}{2N}}$$

For  $p$  even,  $\sin^2(p/2)$  vanishes, for  $p$  odd however,  $\sin^2(p/2) = 1$ . Therefore, the relation (10) is also verified in a good approximation.

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## NOTE

After preparing this text to print the author has read in Physical Review Letters the summary of an article by R. Orbach and P. Pincus, to be published in Physical Review and treating the same problem. It is to be hoped, that the results of Mrs Orbach and Pincus will agree in principle with our results.



## FERRIMAGNETIC SPIN-WAVE RESONANCE

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The purpose of the present paper is the theoretical investigation of the possibility of exciting spin wave modes in ferrimagnetics by an uniform rf field. Ferrimagnetics with parallel spins as well as those with antiparallel spins have been considered. The resonance values of applied magnetic field for allowed odd modes of spin waves and for a given value of the frequency of rf magnetic field are obtained. For even modes the resonances do not appear provided that eddy currents can be neglected and that spin waves have nodes at the boundaries. In the special case of ferromagnetics one gets the formula of Kittel (*Phys. Rev.*, **110**, 1295 (1958)) and in the case of antiferromagnetics the resonance formula goes over into that derived by Cofta (*Acta phys. Polon.* **97**, 187 (1960)). The author estimates also the interval between successive odd mode peaks.

*Introduction*

In the past year Kittel (1958) has investigated theoretically the possibility of exciting exchange modes of spin waves in ferromagnetics by an uniform radio-frequency magnetic field. He showed that such effects may occur in thin specimens. In this manner a new resonance phenomenon, called "spin-wave resonance", has been discovered by means of theoretical research. Seavey and Tannenwald (1958) have observed the spin-wave resonances for a permalloy film of 5600 Å thickness. These experiments have confirmed Kittel's results; as predicted, pronounced peaks occur for odd modes only.

The direct observation of spin-wave resonances at room temperature shows that the spin waves method, even in the simple semiclassical form as used by Kittel, is a good approach to the theory of ferromagnetism for an unexpectedly large range of temperatures. Moreover, from such measurements one can obtain the value of exchange integral.

On account of these reasons it should be very interesting to extend the theoretical discussion of spin-wave resonance to a larger class of magnetic materials. An attempt

of such a discussion for the case of antiferromagnetics has been made recently by Orbach and Pincus (1959) and independently by Cofta (1960).

In a simplified manner analogous to that of Kittel's quoted work, we shall consider in the present paper the general case concerning all substances for which a significant exchange coupling between atomic spins exists, inducing an arrangement of spin orientations. We shall call all such substances "ferrimagnetics" and include here these with parallel spins as well as these with antiparallel ones. When all spins have the same value and are arranged parallelly — we have the case of ferromagnetism; however for antiparallel orientation of such spins — we have the case of antiferromagnetism. For both these special cases the resonance formula derived in our paper goes over into ferromagnetic or antiferromagnetic formula respectively, both derived in the papers<sup>1</sup> mentioned above (Kittel 1958, Cofta 1960).

It is perhaps worth while to remark that permalloy, which has been used by Seavey and Tannenwald (1958), is strictly speaking a ferrimagnetic.

### Calculations

We shall use here the semiclassical method similar to that of Kittel (1958). Some modifications introduced have been discussed in our previous article (Cofta 1960).

We shall consider a ferrimagnetic chain of spins, which is directed perpendicularly to the plane faces of a plate. Let us assume, that the chain contains  $N$  spins of two kinds, aligned alternately in the equal distances  $a$ . In a cartesian coordinates system we can write the equation of motion for  $m$ -th spin  $\mathbf{S}_m$  of the considered chain as follows

$$\hbar \dot{\mathbf{S}}_m = \mathbf{S}_m \times \{ \hbar \gamma \mathbf{G}_m + 2J(\mathbf{S}_{m-1} + \mathbf{S}_{m+1}) \} \quad (1)$$

where  $J$  is the exchange integral for nearest neighbours interactions and  $\hbar$  — the Planck's constant divided by  $2\pi$ , the negative constant  $\gamma$  being the magnetomechanical ratio. Let us assume the  $z$ -axis perpendicular to the plate face and denote by  $\mathbf{j}_x$ ,  $\mathbf{j}_y$  and  $\mathbf{j}_z$  respectively the unit vectors of  $x$ ,  $y$  and  $z$ -axis. Then, the vector  $\mathbf{G}_m$  includes all three magnetic fields which we take here into consideration, namely: 1° the applied constant field  $\mathbf{H}$ , directed along the  $z$ -axis; 2° the effective anisotropy field  $\mathbf{H}_{Am}$  which acts on the internal spins also in the  $z$ -direction and may be different for different sublattices; 3° the rf field  $2H_R e^{i\omega t} \mathbf{j}_x$  alternating with a given frequency of order of  $10^4$  Mc/sec or more. We can decompose this field into two circularly polarized components and neglect (Bloch and Siegert 1940) that component which rotates in opposite sense to the spin precession (this point is also discussed by Cofta 1960). Then we have

$$\mathbf{G}_m = \{H^z + (H_{Am})^z\} \mathbf{j}_z + H_R e^{i\omega t} \mathbf{j}$$

where  $\mathbf{j} = \mathbf{j}_x + i\mathbf{j}_y$ .

<sup>1</sup> Writing the present article the author did not know yet the results of Orbach and Pincus (1959). It is to be hoped, that they will agree with the formula for antiferromagnetic special case, derived in the present paper.



When we impose Kittel's (1958) spin pinning boundary condition then the solution of (1) represents a standing wave of spin precession. We write it in the form:

$$\mathbf{S}_m = R_m e^{i\omega t} \mathbf{j} + S_m^z \mathbf{j}_z \quad (2)$$

Substituting (2) into (1) and using the identity

$$\mathbf{j}_z \times \mathbf{j} = -i\mathbf{j}$$

we get the fundamental relation for  $R_m$ :

$$\begin{aligned} R_m \{-\omega + \gamma [H^z + (H_A)_m^z] + \frac{1}{2} \eta [S_{m-1}^z + S_{m+1}^z]\} = \\ = \frac{1}{2} \eta S_m^z (R_{m-1} + R_{m+1}) + S_m^z \gamma H_R \end{aligned} \quad (3)$$

where  $\eta = 4J/\hbar$ . The  $R_m$ ,  $S_m^z$  and  $(H_A)_m^z$  are different for different sublattices; therefore we put for the first one:

$$S_m^z = A^z, \quad R_m = \sum_p a_p \sin ak_p m, \quad (H_A)_m^z = H_1^z$$

and for the second one:

$$S_m^z = B^z, \quad R_m = \sum_p b_p \sin ak_p m, \quad (H_A)_m^z = H_2^z$$

where the wave number  $k_p = \pi p/aN$  on account of Kittel's boundary condition. Moreover, we have to put  $H^z = -H$ . Hence, we get for each sublattice a relation of the same form:

$$\sum_p c_p \sin ak_p m = \gamma H_R \quad (4)$$

but we have

$$A^z c_p = a_p [-\omega + \gamma (H_1^z - H) + \eta B^z] - b_p \eta A^z f_p \quad (5)$$

for the first sublattice and

$$B^z c_p = b_p [-\omega + \gamma (H_2^z - H) + \eta A^z] - a_p \eta B^z f_p \quad (6)$$

for the second one,  $f_p$  being the abbreviation for  $\cos ak_p$ .

From (5) and (6) we get:

$$C_p = a_p \frac{Q_p}{L_p} = b_p \frac{Q_p}{M_p} \quad (7)$$

where

$$\begin{aligned} Q_p &= [-\omega + \gamma (H_1^z - H) + \eta B^z] [-\omega + \gamma (H_2^z - H) + \eta A^z] - A^z B^z \eta^2 f_p^2 \\ L_p &= A^z [-\omega + \gamma (H_2^z - H) + \eta A^z + \eta B^z f_p] \\ M_p &= B^z [-\omega + \gamma (H_1^z - H) + \eta B^z + \eta A^z f_p] \end{aligned}$$

One can obtain the coefficients  $c_p$  multiplying both sides of (4) by  $\sin q\pi m/N$  and making the summation from  $m = 1$  to  $m = N$  (as to the details see the article of

Cofta 1960). We get:

$$c_p = \begin{cases} 0 & \text{for } p \text{ even} \\ 4\gamma H_R/\pi p & \text{for } p \text{ odd} \end{cases}$$

and therefore from (7) we obtain for  $p$  odd:

$$\begin{aligned} a_p &= \frac{4\gamma H_R}{\pi p} \cdot \frac{L_p}{Q_p} \\ b_p &= \frac{4\gamma H_R}{\pi p} \cdot \frac{M_p}{Q_p} \end{aligned} \quad (8)$$

both these coefficients vanishing for  $p$  even.

### Discussion

The result (8) shows that when the spin pinning boundary condition is fulfilled and it is possible to neglect eddy currents, then the odd mode peaks only can be expected. As can be seen from (8), resonance occurs for  $Q_p = 0$ . Taking  $\omega$  constant we get quadratic equation for  $H$ , from which we obtain the resonance values of applied field for allowed modes:

$$\begin{aligned} H_p = H_\omega + \frac{1}{2} (H_1^z + H_2^z) + \frac{1}{2} (\eta/\gamma) (A^z + B^z) \pm \frac{1}{2\gamma} \{ [\eta (A^z - B^z) + \\ + \gamma (H_2^z - H_1^z)]^2 + 4 A^z B^z \eta^2 \cos^2 ak_p \}^{1/2} \end{aligned} \quad (9)$$

where  $H_\omega = -\omega/\gamma > 0$ . For low values of  $p$  we have to write:

$$H_p = H_\omega + \kappa \pm \frac{1}{2} \sqrt{\alpha - \beta p^2} \quad (10)$$

where

$$\begin{aligned} \kappa &= \frac{1}{2} (H_1^z + H_2^z) + \frac{1}{2} (\eta/\gamma) (A^z + B^z) \\ \alpha &= (\eta/\gamma)^2 (A^z + B^z)^2 + 2(\eta/\gamma) (A^z - B^z) (H_2^z - H_1^z) + (H_2^z - H_1^z)^2 \\ \beta &= 4A^z B^z (\eta/\gamma)^2 \pi^2/N^2 \end{aligned} \quad (11)$$

Now we shall consider the special forms of derived formula for various cases.

#### 1. The case of ferromagnetism

In this case we have to put  $A^z = B^z = S$  and  $H_1^z = H_2^z = -H_A$ . Then, introducing the abbreviation

$$H_E = |\eta/\gamma| \quad (12)$$

we get from the appropriate branch of (10):

$$H_p = H_\omega - H_A - \frac{1}{2} H_E \pi^2 p^2/N^2 \quad (13)$$

which agrees with Kittel's (1958) result<sup>1</sup>.

<sup>1</sup> The double sign  $\pm \omega$  before the applied radio-frequency appearing in Kittel's formula is caused by the iterating procedure used by this author.

## 2. The case of antiferromagnetism

Here we have to put  $A^z = -B^z = S$  and  $H_1^z = -H_2^z = -H_A$ .

Then

$$H_p = H_\omega \pm [H_A (H_A + 2H_E) + H_E^2 \pi^2 p^2 / N^2]^{1/2} \quad (14)$$

which is identical with the result of Cofta (1960).

## 3. The case of ferrimagnetism with parallel spins.

In this case we put:  $A^z = S_1$ ,  $B^z = S_2$  and  $H_1^z = -H_1$ ,  $H_2^z = -H_2$ .

Then we get for (10):

$$\begin{aligned} \kappa &= -\frac{1}{2} (H_1 + H_2) + \frac{1}{2} (\eta/\gamma) (S_1 + S_2) \\ \alpha &= (\eta/\gamma)^2 (S_1 + S_2)^2 + 2(\eta/\gamma) (H_1 - H_2) (S_1 - S_2) + (H_1 - H_2)^2 \\ \beta &= +4(\eta/\gamma)^2 S_1 S_2 \pi^2 / N^2 \end{aligned} \quad (15)$$

## 4. The case of ferrimagnetism with antiparallel spins (antiferromagnetism).

We put:  $A^z = S_1$ ,  $B^z = -S_2$ ,  $H_1^z = -H_1$ ,  $H_2^z = H_2$ , getting for (10):

$$\begin{aligned} \kappa &= \frac{1}{2} (H_2 - H_1) + \frac{1}{2} (\eta/\gamma) (S_1 - S_2) \\ \alpha &= (\eta/\gamma)^2 (S_2 - S_2)^2 + 2(\eta/\gamma) (H_1 + H_2) (S_2 + S_2) + (H_2 + H_2)^2 \\ \beta &= -4(\eta/\gamma)^2 S_2 S_2 \pi^2 / N \end{aligned} \quad (16)$$

For both cases of ferrimagnetism (case 3. and 4.) we have  $\alpha \gg \beta p^2$  for small  $p$  values and  $N \sim 10^3$ ; consequently we can expand the square root in (10). Then; we get the resonance formula (10) in the form

$$H_p \approx H_\omega + \kappa \mp \frac{1}{2} \alpha^{1/2} \pm \frac{1}{4} \beta \alpha^{-1/2} p^2 \quad (17)$$

similar to that for the case of ferromagnetism.

As can be seen, in cases 2., 3. and 4. we have two resonance series, because for each  $p$  two resonance values occur, separated mutually by  $(\alpha - \beta p^2)^{1/2}$ . In cases 3. and 4. the separation of two peaks corresponding to the same value of  $p$  may be written approximately:

$$|H'_p - H''_p| \approx \alpha^{1/2} - \frac{1}{2} \beta \alpha^{-1/2} p^2 \quad (18)$$

Let us now estimate the interval

$$\Delta H = |H_{p+2} - H_p|$$

between two successive odd mode peaks of the same series. Using the abbreviation (11) we can write for low values of  $p$ :

$$\begin{aligned} \Delta H &= \frac{1}{2} |[\alpha - \beta (p+2)^2]^{1/2} - [\alpha - \beta p^2]^{1/2}| \\ &\approx |\beta| (\alpha - \beta p^2)^{-1/2} (p+1) \end{aligned}$$

Let us put:  $S_1 = S$ ,  $S_2 = \lambda S$ , where usually  $\frac{1}{2} \leq \lambda \leq 1$  Considering not too thin plates ( $N \sim 10^3$ ) and neglecting the generally small effects of anisotropy fields, we

have approximately for the lowest modes ( $p < 10$ ):

$$\alpha - \beta p^2 \sim H_E^2 (1 + \lambda)^2$$

for the case of parallel spins and

$$\alpha - \beta p^2 \sim H_E^2 (1 - \lambda)^2 + 4H_E H_A (1 + \lambda)$$

for the case of antiparallel spins, where  $H_E$  is defined by (12). Hence for parallel spins the considered interval is

$$\Delta H \approx 4H_E \frac{\lambda}{1 + \lambda} \cdot \frac{\pi^2}{N^2} (p + 1) \quad (19)$$

which goes over into

$$2H_E \frac{\pi^2}{N^2} (p + 1)$$

for the case of ferromagnetism ( $\lambda = 1$ ). For antiparallel spins however we get

$$\Delta H \approx \frac{4H_E \lambda}{[(1 - \lambda)^2 + 4(1 + \lambda) H_A/H_E]^{1/2}} \cdot \frac{\pi^2}{N^2} (p + 1) \quad (20)$$

which goes over into

$$\frac{2H_E}{\sqrt{2H_A/H_E}} \cdot \frac{\pi^2}{N^2} (p + 1)$$

for the case of antiferromagnetism ( $\lambda = 1$ ).

### Acknowledgments

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### NOTE ADDED IN PROOF

The article on antiferromagnetic spin-wave resonance by Orbach & Pincus has appeared in *Phys. Rev.* **113**, 1213 (1959). The results obtained by these authors are quite the same as those shown in the formula (14). The author is greatly indebted to Dr. R. Orbach and Dr. P. Pincus for kindly sending the informations on their publication prior to coming of No. 5 (March 1, 1959) of the *Physical Review* to Poznań.



## DECAY OF PHOSPHORESCENCE OF TRYPAFLAVINE IN GELATINE

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The absorption spectra and decay curves of phosphorescence of tryptaflavine in gelatine were investigated as a function of the pH value of the aqueous tryptaflavine solution in which the gelatine has been coloured. It appeared that they vary with pH of the above solution. The observed decay curves and their decomposition into simple exponential functions can be explained assuming the tryptaflavine molecule to exhibit one metastable level only and by taking into account the observed preexcitation effects.

### *Introduction*

The aim of the present paper is to check on ground of investigation of the decay curves of phosphorescence of tryptaflavine in gelatine, whether this dye exhibits more than one metastable level.

On ground of investigations on the decay curves of phosphorescence of tryptaflavine adsorbed on silicagel (Pringsheim and Vogel 1936) and on observations on oxygen quenching, the tryptaflavine molecule was supposed to possess two metastable levels (Pringsheim and Franck 1943a). Similar suggestions were put forward from considerations of the observed variations of the polarization rate in various spectral ranges of the phosphorescence and slow fluorescence bands (Pilipovitch and Sveshnikov 1958a), of deviations of phosphorescence decay from the exponential law, and of the dependence of the slow fluorescence decay constant on the wavelength within the emitted band (Pilipovitch and Sveshnikov 1958b).

Molecules, for which investigations carried out hitherto have lead to ascribe them more than one metastable level, are assembled in Table I.<sup>1</sup> However, the interpretation of the above facts is by no means unequivocal. Thus, e. g. Bre-

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<sup>1</sup> The structure of the dye molecules given in Table I is to be found in Pringsheim and Vogel's "Luminescence of Liquids and Solids" (1943b), and in Foerster's "Fluoreszenz organischer Verbindungen" (1951).

TABLE I

Some dyes supposed to possess more than one metastable level

No.	Dye	Substratum	Author
1	Trypaflavine	Silicagel	Pringsheim, P., Vogels, H., 1936
		Sugar	Pringsheim, P., Frank, J., 1943
			Pilipovitch, V. A., Sveshnikov, B. I. 1958 a, 1958 b
2	Fluoresceine	Boric acid	Pilipovitch V. A., Sveshnikov B. I., 1958b
		Sugar	Pilipovitch V. A., Sveshnikov B. I., 1958 a
3	acridine orange	Sugar	Pilipovitch V. A., Sveshnikov B. I., 1958 b
4	esculin	Sugar	Pilipovitch V. A., Sveshnikov B. I., 1958 b
5	auramine	Sugar	Pilipovitch V. A., Sveshnikov B. I., 1958 b
6	carbosol	Sugar	Pilipovitch V. A., Sveshnikov B. I., 1958 a
7	eosine	Sugar	Pilipovitch V. A., Sveshnikov B. I., 1958 a

del (1955) explains the deviations from the exponential law observed in the decay of phosphorescence of fluoresceine in boric acid by a hypothesis due to Tomaschek (1922). The electronic terms of the dye molecule and the probabilities of electron transitions connected with phosphorescence emission can vary as a result of interactions between the dye molecule and its surroundings. The interactions may be different in the case of various molecules. Hence phosphorescence becomes a complex process and its decay will no longer be described by a purely exponential law. These deviations can also be explained, i. a., by a simplified model of luminescent centres as proposed by Jabłoński (1957a).

Quite generally, the interpretation of the observed luminescence phenomena depends largely on whether differences in the nearest surroundings of the various luminescent molecules are taken into account or not. This is a point that is especially critical in the various theories of photoluminescence. The last standpoint is represented by theories put forward by Vavilov (1942, 1943, 1944, 1950, Feofilov and Vavilov 1931, Shishlovsky and Vavilov 1934), whilst the other is that of Jabłoński's theory of luminescent centres (1936, 1954, 1955, 1957a), by which the observed phenomena should be generally considered as the superposition of phenomena occurring within the various groups of centres. In very special cases only do both theoretical approaches yield the same form for photoluminescence decay.

The above differences in theoretical approach are practically of little consequence for the problem of the dependence of photoluminescence yield on the concentration of the quenching molecules (Förster 1949, Galanin 1955<sup>2</sup>, Jabłoński 1957 b).

<sup>2</sup> Rozman (1958) proved the theories of Förster (1949) and of Galanin (1955) to be identical.

So far, no suggestions have been made on the possibility of solving the problem of multitude of metastable levels on ground of investigations of the dependence on concentration of the luminescence yield.

On the other hand, Kislak (1958, 1959), who investigated the slow fluorescence decay of above organophosphors, has found it to be strictly exponential. This amounts to assuming that a single metastable level is responsible for the slow fluorescence observed by this autor.

It seems to be a problematic question whether there are or not two metastable levels in trypaflavine as well as in fluoresceine. The aim of this paper is to elucidate this question.

### *Experimental*

The decay curves of trypaflavine in gelatine were investigated with a "linear" phosphoroscope. A phosphor having the shape of an "driving belt" was set in motion. A part of its path was rectilinear. In this segment of the path, the phosphor was excited and the decay of phosphorescence measured. An appropriate system of slits served to separate the exciting and scattered light from that of the luminescence measured. The phosphorescence light was photographed through a polaroid. By orienting the latter with respect to the direction of the electric vector of the plane polarized exciting light, it was possible to obtain successively photographs of both the  $I_{\perp}$  (perpendicular) and  $I_{\parallel}$  (parallel) components of phosphorescence. A detailed description of the "linear" phosphoroscope is given in an earlier paper (Frąckowiak 1957a).

The phosphorescence decay curves were measured in the following conditions:

- 1) velocity of displacement of phosphor:  $1155 \pm 60$  cm/sec,
- 2) duration of excitation:  $2,16 \times 10^{-4}$  sec,
- 3) observation of the decay curves started  $4,76 \times 10^{-4}$  sec, after cessation of excitation and lasted until  $10^{-2}$  sec,
- 4) duration of exposition was 30 sec,
- 5) measurements were carried out at room temperature ( $20^{\circ}\text{C}$ ).

The phosphor was excited with plane polarized white light. Both components of the decay curves were investigated throughout the entire band of luminescence.

The phosphors were prepared as follows: Unexposed fixed and dried "Ultra-rapid" films of equal length were kept in appropriate aqueous trypaflavine solutions for an hour, and subsequently rinsed in flowing water for 10 minutes. After drying, the decay curves were investigated. The trypaflavine concentrations in the phosphors were determined from the absorption bands, which were measured with a Zeiss spectrophotometer.

The above mentioned trypaflavine solutions were prepared as follows: 27,7 mg and 277,7 mg of trypaflavine were dissolved in equal volumes of distilled water, of 0,1 *n* HCl solution, and of 0,1 *n* KOH solution. Thus, solutions of known trypaflavine

concentrations and different pH were obtained. The latter was measured with a PHM — 3i pH-meter. The absorption spectra of the aqueous tryptaflavine solutions were measured with a Zeiss spectrophotometer.

All data relating to the solutions and tryptaflavine concentration in the phosphors are given in Table II.

TABLE II

Quantities characteristic of aqueous tryptaflavine solutions, and concentration in gelatine

No. of solution	Aqueous solutions				Solutions in gelatine Tryptaflavine concentration mol/l
	Solvent	Tryptaflavine concentration $\times 10^{-3}$ mol/l	pH	$\gamma$	
1	0,1 n HCl	0,106	1,0	7,38	
2		1,066	0,5	2,44	0,0071
3	distilled water	0,106	4,6	1,0	0,045
4		1,066	7,9	0,93	0,444
5	0,1 n KOH	0,106	12,5	2,66	0,057
6		1,066	10,2	0,87	0,436

### Experimental Results

Fig. 1 shows the extinction coefficients as a function of wavelength, for tryptaflavine in the solutions used for impregnating gelatine with the dye. All extinction curves in Fig. 1 have the same area, i. e. the total "intensity of absorption" is equal. By comparing these areas with that of a band for an arbitrarily chosen concentration, the relative value of the factor  $\gamma$  in the generalized expression for the oscillator strength (Proter and Windsor 1958), accounting for interaction between the absorbing molecule and the medium, can be determined:

$$f = \frac{mc^2}{\pi e^2 N} \int_0^\infty \gamma \epsilon_\nu d\nu \approx \gamma \frac{mc^2}{\pi e^2 N} \int_0^\infty \epsilon_\nu d\nu = \gamma f_0 \quad (1)$$

where  $f$  — denotes the oscillator strength,

$m$  — the mass of the electron,

$c$  — the velocity of light,

$e$  — elementary charge,

$N$  — the number of absorbing molecules per  $1 \text{ cm}^3$  of the solution, and

$\epsilon$  — the extinction coefficient.

For the lower concentration of the tryptaflavine in distilled water  $\gamma = 1$  ( $f = f_0$ ) was assumed. The values of  $\gamma$  for different solutions are given in Table II.



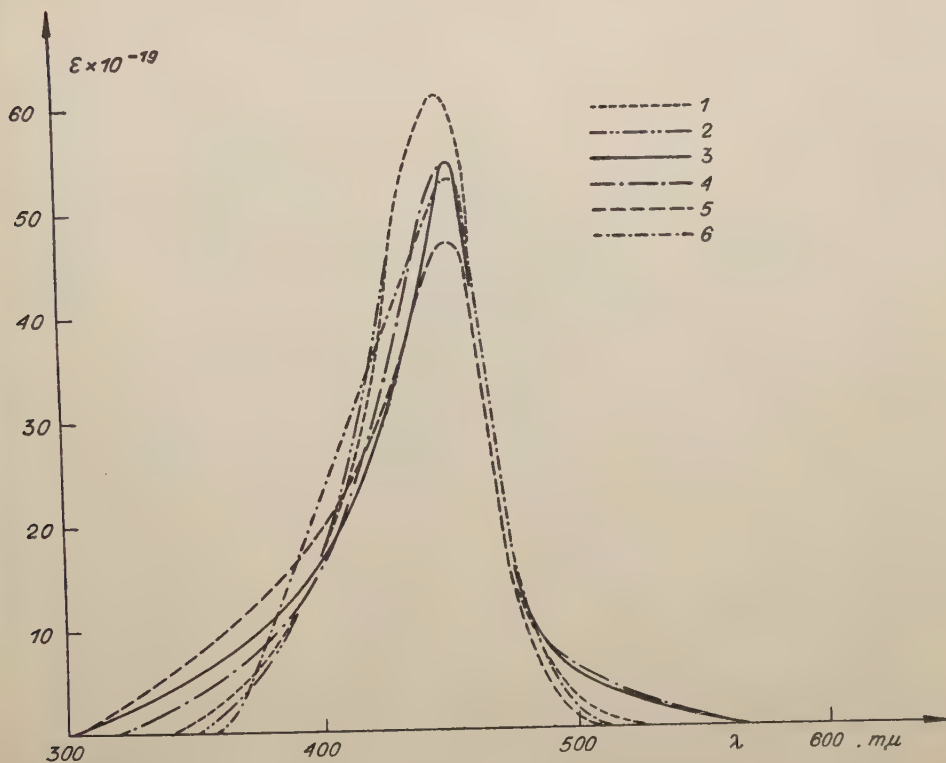


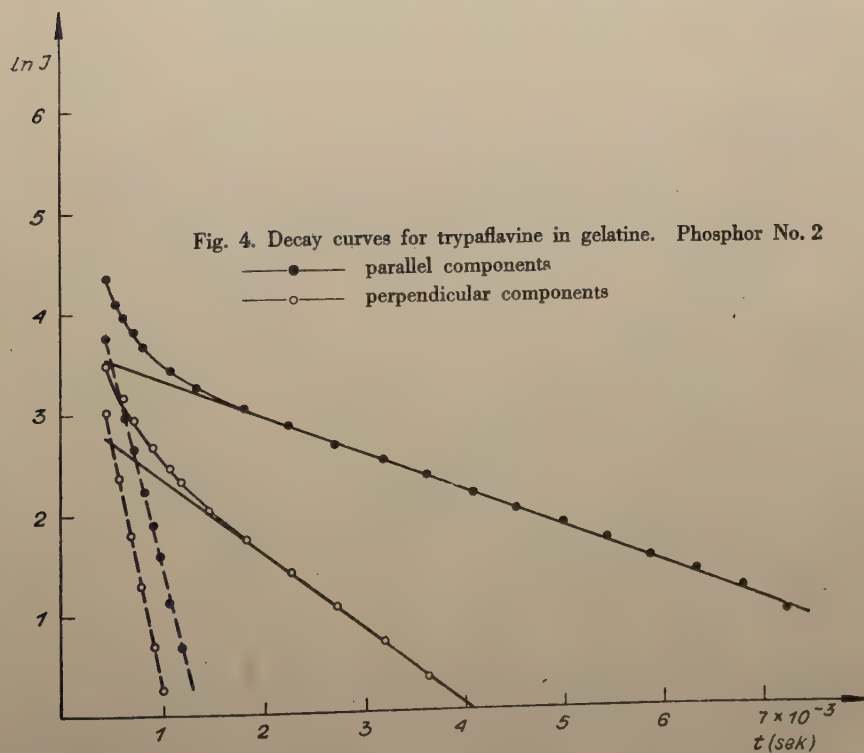
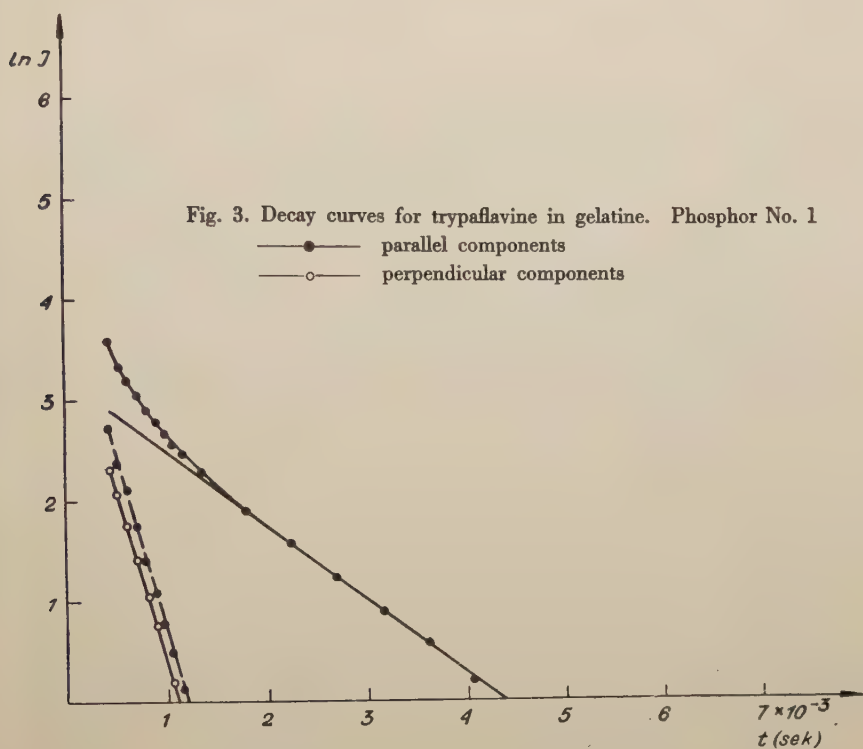
Fig. 1. Absorption spectra of aqueous trypaflavine solutions.

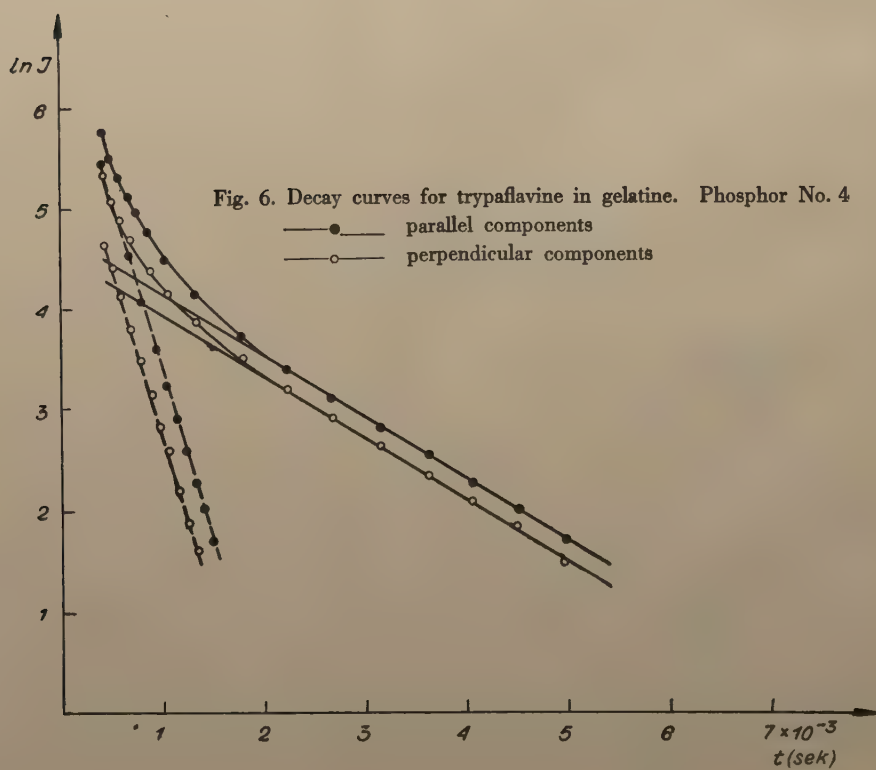
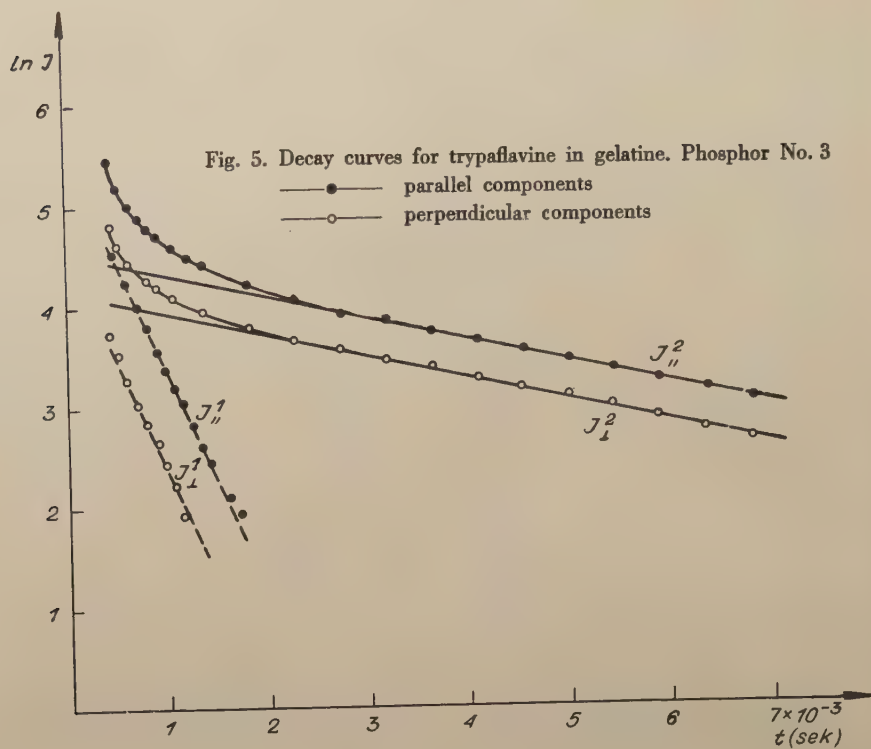
-----	Solution No. 1	
-. - . - . - . - . - .	" 2	} see Table II
—————	" 3	
— . . — . . — . . — . .	" 4	
-----	" 5	
-. - . - . - . - . - .	" 6	

Fig. 2 shows curves for the absorption band of trypaflavine in gelatine. These have been "normalized" as in the case of the aqueous solutions. From these absorption bands, the concentrations  $C$  of trypaflavine were determined, as given in Table II. It should be stressed that the  $C$  values do not necessarily coincide with the true concentrations of trypaflavine in gelatine. As the swelling process takes place in media with different pH, gelatine can exhibit different properties (cf. Basiński, "Physical Chemistry of Colloids" 1957). These variations can lead to variations in the interaction between trypaflavine and gelatine, and, hence, to variations in the value of the factor  $\gamma$  in eq. (1). Hence, determining the concentration from the absorption bands, with the approximation of eq. (1), yields but a value  $C^*$  equal to

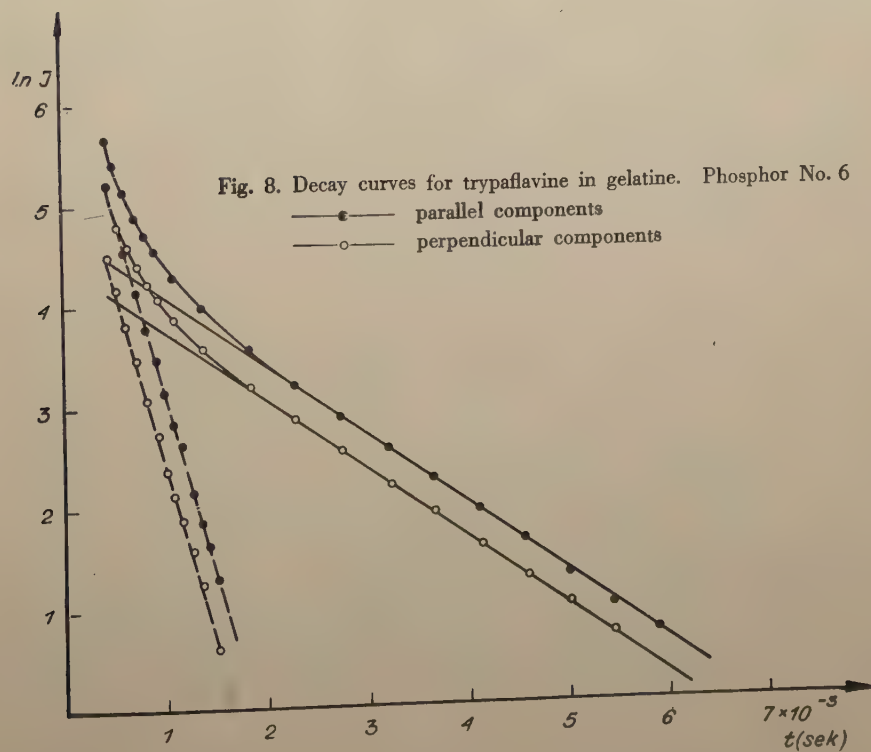
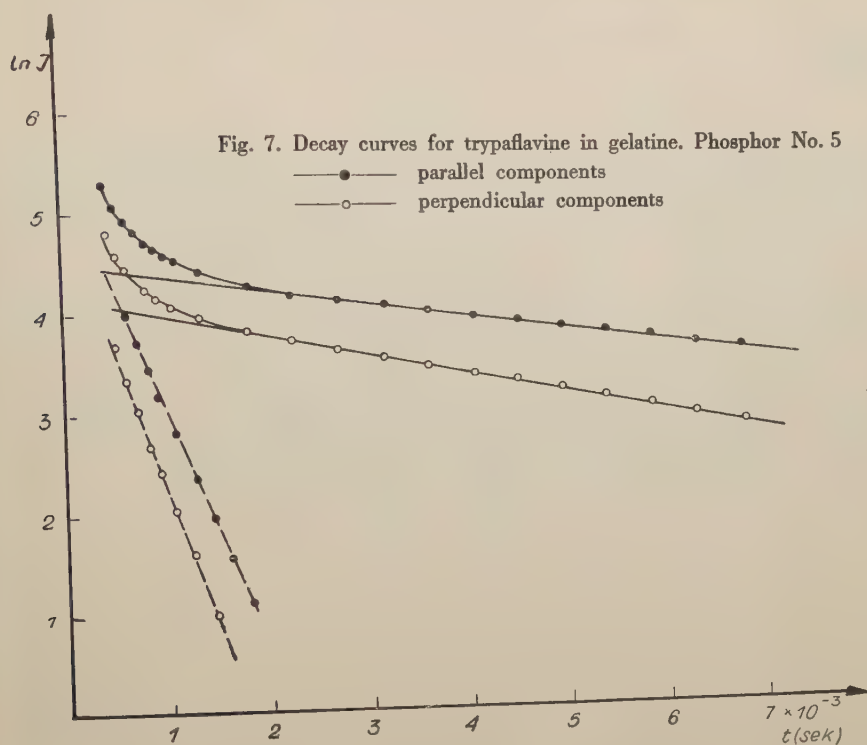
$$C^* = \gamma C, \quad (2)$$











Hence the time dependence of the total phosphorescence intensity emitted in all directions is:

$$I(t) = I_{||}(t) + 2I_{\perp}(t) = 3[A_1 \exp(-\varphi_1 t) + A_2 \exp(-\varphi_2 t)]; \quad (4)$$

the values of the constants are assembled in Table III.

TABLE III

Constants of phosphorescence decay, emission anisotropies, and initial phosphorescence intensities for tryptaflavine in gelatine

No. of solution	Component	Decay constants $\times 10^3 \text{ sec}^{-1}$	Emission anisotropies	Values of $I_{  }$ and $I_{\perp}$ at $t = 0$
1	$I_{  }^1$	34,0	—	75
	$I_{\perp}^1$	—	—	—
	$I_{  }^2$	7,3	—	26
	$I_{\perp}^2$	3,3	—	12
2	$I_{  }^1$	40,0	—	245
	$I_{\perp}^1$	50,0	—	215
	$I_{  }^2$	3,8	—	42
	$I_{\perp}^2$	7,5	—	24
3	$I_{  }^1$	22,5	0,232	305
	$I_{\perp}^1$	22,5	—	160
	$I_{  }^2$	2,25	0,139	95
	$I_{\perp}^2$	2,25	—	64
4	$I_{  }^1$	33,5	0,269	1080
	$I_{\perp}^1$	33,5	—	513
	$I_{  }^2$	6,0	0,072	121
	$I_{\perp}^2$	6,0	—	98
5	$I_{  }^1$	24,0	—	267
	$I_{\perp}^1$	27,5	—	165
	$I_{  }^2$	1,4	—	90
	$I_{\perp}^2$	2,0	—	64
6	$I_{  }^1$	36,0	0,273	1050
	$I_{\perp}^1$	36,0	—	493
	$I_{  }^2$	6,8	0,120	124
	$I_{\perp}^2$	6,8	—	88

The decay curves for the phosphors impregnated in solutions Nos. 1, 2 and 5 (Figs. 3, 4 and 7) cannot be represented by means of eqs. (3) and (4). For these phosphors, Table III brings only the respective decay constants  $\varphi$  and the values of  $A$ .

### Discussion

Trypaflavine in gelatine is a two-phase substratum organophosphor, resembling a colloidal solution (Fröhlich and Mischung 1944). This dye, according to the hypothesis of Pringsheim et al. (Pringsheim and Vogels 1936, Pringsheim and Franck 1943, Pilipovitch and Sveshnikov 1958a, 1958b), should exhibit two metastable levels. Investigation of the decay curves for trypaflavine in gelatine impregnated in solutions of type 4 and 5 (Table II) throughout the range of low concentrations ( $10^{-5}$  to  $10^{-3}$  mol/l) yielded a shape of phosphorescence decay similar to that observed at high concentrations  $10^{-2}$  to  $10^{-1}$  mol/l) as shown in Figs. 5 and 6. The fact that for low as well as for high concentrations of trypaflavine in gelatine the decay curves can be decomposed into two exponential functions only points to independence of this decomposition from any interaction whatever between the excited luminescent molecule and other, non-excited ones, in its neighbourhood (Frackowiak 1957a, 1957b). According to Förster (1946), trypaflavine in aqueous solutions forms associates. To determine whether such associates can be made to account for the decompositions of the decay curves as observed in the present investigation, a comparison was made of the absorption spectra of aqueous and gelatine solutions of trypaflavine. As seen in Fig. 1, for aqueous solutions of trypaflavine, the changes characteristic of associates in the absorption bands do not appear (Kraviets, Pyeskina and Zitkova 1950, Levshin and Baranova 1956, 1958, Förster and Koenig 1957). Thus, it may be assumed that in the solutions used for impregnating gelatine with trypaflavine practically only monomers were present.

A similar conclusion is reached on investigating the changes in the absorption of trypaflavine in gelatine as shown in Fig. 2, with exception of curve No. 6. Even if trypaflavine dimers were to account for the "splitting" of this band, they would still have nothing to do with the observed composition of the decay curves, since the shape of the curves for the phosphor under consideration (Fig. 8) resembles that obtained with phosphors (Figs. 5 and 6) whose absorption bands exhibit no corresponding changes.

It is seen from Table II that the concentrations  $C^*$  of trypaflavine in gelatine impregnated with solutions of different pH values are different, notwithstanding the fact that impregnation had been carried out in identical conditions. This circumstance, and also the changes in the absorption bands of Fig. 2 point to changes in the properties of gelatine resulting from immersion in solutions of different pH values. These are changes that can lead to variations in the shape of the phosphorescence decay curves. It will be shown below that the decay of the phosphorescence of trypaflavine in gelatine follows one general law enabling to describe all observed shapes of the decay curves from the properties of the gelatine.

All the decay curves of Figs. 3, 4, 5, 6, 7 and 8 (and their decompositions) can be

accounted for assuming tryptaflavine decay in gelatine to be described by the following expressions:

$$I_{||}(t) = \sum_{i=1}^4 B_i (1 + 2r_i) \exp(-\Gamma_i t) \quad (5)$$

$$I_{\perp}(t) = \sum_{i=1}^4 B_i (1 - r_i) \exp(-\Gamma_i t)$$

$$I(t) = I_{||}(t) + 2I_{\perp}(t) = 3 \sum_{i=1}^4 B_i \exp(-\Gamma_i t) \quad (6)$$

with  $B_i$ ,  $r_i$ , and  $\Gamma_i$  ( $i = 1, 2, 3, 4$ ) denoting certain constants.

A number of simple hypotheses can be proposed which make it possible to describe phosphorescence decay by (5) and (6).

1. The tryptaflavine molecules have two metastable levels and exhibit phosphorescence within both phases of the gelatine.

As well known the medium (substratum) does affect considerably the luminescent properties of dyes (Pringsheim "Fluorescence and Phosphorescence" 1951). If tryptaflavine is phosphorescent in both phases of the gelatine, then the phosphorescence observed is clearly a superposition of two „different” phosphors. Assuming both metastable levels to take part in the process of phosphorescence or in slow fluorescence, we are lead to expressions (5) and (6). Iwaki (1953a, 1953b) found that the constants of phosphorescence decay of tryptaflavine and acridine orange in gelatine decrease as the exciting light intensity rises. Preliminary investigation of the pre-excited state of tryptaflavine in gelatine by the present author showed the intensity of phosphorescence to rise with the time of pre-excitation. Variations of the intensity of the exciting light may be considered to produce effects similar to those of variations of the time of pre-excitation at constant intensity of the exciting light. Thus, e. g. for acridine yellow in gelatine, as pre-excitation rises, a fall in the phosphorescence intensity is observed simultaneously with an increase in its decay constants. The symbol  $P^{+}$  has been employed for denoting such a pre-excited state of the phosphor (Frąckowiak and Heldt 1959). It may be assumed that similar effects occur in tryptaflavine in gelatine. In this case, however, the pre-excited state is  $P^{+-}$ , meaning that a rise in the intensity of phosphorescence is accompanied by a fall in the constants of phosphorescence decay.

This hypothesis, however, does not take into account the effects of pre-excitation mentioned. To account for these, it would need functions of greater complexity than (5) and (6) to describe the decay of phosphorescence. As already mentioned, eqs. (5) and (6) are quite sufficient for description of all decay curves observed (their decompositions into simple exponential functions). For these reasons the foregoing hypothesis can be rejected.

2. The tryptaflavine molecules have two metastable levels, and are phosphorescent within one of the gelatine phases only, and exhibit pre-excitation effects.

On the assumption that acridine orange, like tryptaflavine, has two metastable levels (Table I), we can expect the decay process of both dyes in gelatine to be similar. In-



vestigation on the subject has in fact proved (Frąckowiak 1957b) the decay curves of acridine orange and yellow in gelatine to wholly resemble one another. Hence, we can compare the decay of phosphorescence in trypaflavine with that in acridine yellow, which exhibits pre-excitation effects (Frąckowiak and Heldt 1959, Waleryś 1959, Frąckowiak, Grzywacz and Heldt 1959). The fact that the experimental decay curves of the phosphorescence of acridine yellow in gelatine (Frąckowiak 1957a, 1957b) agree well with the theoretical curves for homogeneous rigid solutions (Jabłoński 1957a) indicates that acridine yellow does phosphoresce in one of the two phases of the gelatine. It is easy to state that the phosphorescence decay of trypaflavine in gelatine differs fundamentally from that of acridine yellow. Hence also this hypothesis can be rejected.

3. The trypaflavine molecules have one metastable level, are phosphorescent within both phases of the gelatine, and exhibit pre-excitation effects. This hypothesis yields an explanation of all decay curves as observed for trypaflavine in gelatine.

Let indices  $i = 1, 2$  in eqs. (5) and (6) denote non-deformed and deformed molecules within the first phase of the gelatine, respectively, and  $i = 3, 4$  the respective molecules within the second phase. Moreover, let  $\Gamma_i$  denote the respective decay constants,  $B_i$  — the phosphorescence intensities at the time of cessation of pre-excitation, and  $r$  — the emission anisotropies.

Investigations on the pre-excited state of acridine yellow in gelatine (Frąckowiak and Heldt 1959, Waleryś 1959) have shown that the decay constants of the non-deformed and the deformed centres are different. Trypaflavine centres may be assumed to have similar properties. Since these centres are situated within two distinct media, it may be assumed that  $\Gamma_1 \neq \Gamma_2 \neq \Gamma_3 \neq \Gamma_4$ , and moreover  $\Gamma_1 > \Gamma_2$  and  $\Gamma_3 > \Gamma_4$ , because the pre-excited state is expected to be  $P^{+-}$ .

Let

$$\begin{aligned} B_2 &= k B_1, & m(1 + 2r_1) &= 1 + 2r_2, & m'(1 - r_1) &= 1 - r_2 \\ B_4 &= l B_3, & n(1 + 2r_3) &= 1 + 2r_4, & n'(1 - r_3) &= 1 - r_4 \end{aligned} \quad (7)$$

For  $(\Gamma_1 - \Gamma_2)t \ll 1$  and  $(\Gamma_3 - \Gamma_4)t \ll 1$ , eqs. (5) become

$$\begin{aligned} I_{||}(t) &= B_1(1 + 2r_1)(1 + mk) \exp\left(-\frac{mk\Gamma_2 + \Gamma_1}{mk + 1}t\right) + \\ &+ B_3(1 + 2r_3)(1 + nl) \exp\left(-\frac{n\Gamma_4 + \Gamma_3}{nl + 1}t\right), \\ I_{\perp}(t) &= B_1(1 - r_1)(1 + m'k) \exp\left(-\frac{m'k\Gamma_2 + \Gamma_1}{m'k + 1}t\right) + \\ &+ B_3(1 - r_3)(1 + n'l) \exp\left(-\frac{n'l\Gamma_4 + \Gamma_3}{n'l + 1}t\right). \end{aligned} \quad (8)$$

If the emission anisotropy of the deformed and non-deformed molecules differ but

insignificantly,  $r_1 \approx r_2$  and  $r_3 \approx r_4$ , then (cf. eq. (7))  $m = m' = 1$ ,  $n = n' = 1$ , and eqs. (8) assume the form

$$\begin{aligned} I_{\parallel}(t) &\approx B_1(1 + 2r_1)(1 + k) \exp\left(-\frac{k\Gamma_2 + \Gamma_1}{k + 1}t\right) + \\ &\quad + B_3(1 + 2r_3)(1 + l) \exp\left(-\frac{l\Gamma_4 + \Gamma_3}{l + 1}t\right), \\ I_{\perp}(t) &\approx B_1(1 - r_1)(1 + k) \exp\left(-\frac{k\Gamma_2 + \Gamma_1}{k + 1}t\right) + \\ &\quad + B_3(1 - r_3)(1 + l) \exp\left(-\frac{l\Gamma_4 + \Gamma_3}{l + 1}t\right). \end{aligned} \quad (9)$$

With

$$\begin{aligned} A_1 &= B_1(1 + k), \quad r_1 = r, \quad \varphi_1 = \frac{k\Gamma_2 + \Gamma_1}{k + 1}, \\ A_2 &= B_3(1 + l), \quad r_3 = r', \quad \varphi_2 = \frac{l\Gamma_4 + \Gamma_3}{l + 1}, \end{aligned} \quad (10)$$

eqs. (9) reduce to eqs. (3). As already mentioned eqs. (3) account for phosphorescence decay in phosphors impregnated by means of solutions Nos. 3, 4 and 5 (Figs. 5, 6 and 8). It may be concluded that in these phosphors the emission anisotropies of the deformed and non-deformed molecules differ insignificantly in both phases of the gelatine.

The ratio of the phosphorescence intensities of the nondeformed and the deformed molecules is proportional to the ratio of their numbers, and thus inversely proportional to the probability of the formation of deformed molecules,  $\lambda$ . As already mentioned, the substratum can affect various physical properties of the luminescent molecules, and thus, also the probability  $\lambda$ . Changes in the properties of the substratum generally produce variations of the physical quantities mentioned. Hence, for the two distinct phases of the gelatine,  $\lambda$  must be different:  $\lambda_1$  and  $\lambda_2$ . Since  $k \sim 1/\lambda_1$  and  $l \sim 1/\lambda_2$ , and by eqs. (10),  $\varphi_1 = \varphi_1(k)$ , and  $\varphi_2 = \varphi_2(l)$ , we have  $\varphi_1 = \varphi_1(\lambda_1)$  and  $\varphi_2 = \varphi_2(\lambda_2)$ . From Tables III and II it is seen clearly that equal changes of the pH value of the solutions used for impregnating the phosphors give rise to different changes of  $\varphi_1$  and  $\varphi_2$ . Hence it is to be concluded that, when gelatine is immersed in media of different pH, the two phases change their properties in a different manner. These changes, in turn, affect the emission anisotropies  $r$  and  $r'$  (cf. Tables III and II). The considerable differences in emission anisotropy  $r$  and  $r'$  (Table III) can be explained by the assumption that, in addition to phosphorescence, tryptaflavine at room temperature emits slow fluorescence which is relatively intense in one of the gelatine phases and weak in the other one. In this case  $r$  and  $r'$  should be considered to represent the

emission anisotropies of the total luminescence of the molecules present in the respective media.

The decay curves of trypaflavine in gelatine impregnated with solutions Nos. 1, 2, and 5 (Table II) can be described by eq. (8) only. In these cases, decomposition of the decay curves yields exponential functions of various decay constants. From eqs. (7) this seen to relate to situations when the emission anisotropies of the non-deformed and deformed molecules are different.

It should seem, however, that the quantities  $m$ ,  $n$  and  $m'$ ,  $n'$  (see eqs. (7)) are not related to the properties of the gelatine. From Tables III and II, the decay curves are seen to be described by eqs. (9) or (3) in all cases when the gelatine had been impregnated in solution for which  $\gamma \ll 1$ . This means that the emission anisotropies of the non-deformed and deformed molecules differ but insignificantly if interaction between the trypaflavine molecules and the medium in aqueous solutions is relatively weak. This is in fact the case for solutions, for which  $4 < \text{pH} < 10$ . The decay curves of phosphors impregnated in solutions of pH outside the foregoing range can be accounted for only by eqs. (8). This is the case for phosphors exhibiting different emission anisotropies of the non-deformed and deformed molecules,  $r_1 \neq r_2, r_3 \neq r_4$ , ( $m \neq m' \neq 1$  and  $n \neq n' \neq 1$ ). These had been impregnated in solutions for which  $\gamma \gg 1$ , i. e. in solutions in which interaction between the trypaflavine molecules and the medium was very strong. This interaction could produce some insignificant structural changes in trypaflavine, resulting in insignificant changes in the luminescent properties of the non-deformed molecules but in highly important changes of the respective properties of the deformed molecules. It is known from various investigations (Levis and Bigeleisen 1943) that phosphors consisting of dyes of closely similar structure exhibit greatly different properties in the pre-excited state. Hence it may be concluded that the quantities  $m$  and  $n$  (and  $m'$  and  $n'$ ) in eqs. (7) are related to variations in the structure of the trypaflavine molecule rather than to variations in the properties of the gelatine.

It is seen from Fig. 3 that in the case of phosphor No. 1 the decay curves can be decomposed into three exponential functions only. This is the kind of decomposition to be expected in the present experimental conditions if one of the decay constants in one of exponential functions is, at least, of the order of  $10^5 \text{ sec}^{-1}$ .

In eqs. (5) and (6) fluctuations of the trypaflavine concentration in neither gelatine media were taken into account. Analysis of the decay curves shows that, for trypaflavine in gelatine, the effects produced by interaction between excited and non-excited luminescent molecules (Jabłoński 1957a, Frąckowiak 1957a) are very small as compared to the influence of media on the trypaflavine phosphorescence in two of differences phases of the gelatine. These effects can be accounted for by considering the quantities  $\Gamma_i$ ,  $B_i$  and  $r_i$  ( $i = 1, 2, 3, 4$ ) as averaged over all the appropriate groups of luminescent centres. In this case, the  $\Gamma_i$  and  $r_i$  ( $i = 1, 2, 3, 4$ ) should be expected to vary somewhat with the dye concentration (independently of the pH variations); however, the general character of eqs. (5) and (6) should not change.

*Summary*

The authors investigated the absorption spectra of aqueous and gelatine solutions of tryptaflavine. Monomers of the dye were proved to be practically the only forms present in both cases. The decay curves of phosphorescence of tryptaflavine in gelatine coloured with dye in solution of different pH values were investigated. Three assumptions, of the most simple kind, yielding a consistent account of all decay curves observed and of their composition, are discussed. The hypothesis by which tryptaflavine molecule possesses one metastable level tryptaflavine phosphoresces in both media (phases) of the gelatine, and exhibits pre-excitation effects, is proved to be the most plausible. All decay curves observed are proved to represent special cases within the framework of the foregoing hypothesis. The dependence of the decay curves on the pH values of the solution used for impregnation of the gelatine with the dye are accounted for by changes in the properties of the gelatine. In the cases of solutions having  $\text{pH} > 10$  or  $\text{pH} < 4$ , the shapes of decay curves are also influenced by persistent changes in structure of tryptaflavine molecules produced by media of foregoing pH. The hypothesis proposed can be checked by investigating the pre-excited state of tryptaflavine in gelatine and by studying the spectre of luminescence at various moments following cessation of excitation.

The authors wish to express their indebtedness to Professor Dr A. Jabłoński for his valuable discussions and for his interest throughout the present investigation.

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## INVESTIGATION OF AGEING IN TRIGLYCINE SULFATE

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The evolution in time of the hysteresis loop of  $(\text{NH}_2 \text{ CH}_2\text{COOH})_3\text{H}_2\text{SO}_4$  was investigated. Symples investigated immediately after preparation were found to present a double hysteresis loop.

Only old samples can present double hysteresis loops. The term "old" is used for denoting samples that had not been subjected to investigation of any kind whatsoever, such as heating, an AC field, etc., for a long time. Young samples always exhibit a normal hysteresis loop. The process of converting an old sample into a young one is termed rejuvenation. It can be carried out by heating the sample above the temperature of the Curie point, or by placing it for a time in an AC electric field.

The dielectric properties of triglycine sulfate doped with  $\text{CuSO}_4$  were also investigated. In this case, rejuvenation in an AC field proceeds much more slowly.  $\text{CuSO}_4$  doped triglycine sulfate samples present values of the polarisation  $P_s$  and dielectric permittivity  $\epsilon$  that are lower than the respective values for a sample containing no admixture.

For doped samples, the coercive field depends on the amount of the admixture and rises with its concentration.

### Introduction

Investigation of the ferroelectric properties of triglycine sulfate is due to Matthias, Miller and Remeika (1956). Results of investigations on the dielectric properties of this compound have been published by Hoshino, Mitsui, Jona and Pepinsky (1957), who found a spontaneous polarization of  $P_s = 2,8 \frac{\mu\text{C}}{\text{cm}^2}$  at  $20^\circ\text{C}$ . The Curie point lies at  $48^\circ\text{C}$ . A. G. Chynoweth (1959) found that defects from irradiation produce a decrease in the polarisation. The technology of obtaining large monocrystals of triglycine sulfate, together with results of investigations on their piezoelectric properties (Konstantinova, Sylvestrova Aleksandrov 1959) and pictures of the domain structure (Konstantinova, Sylvestrova, Yureen 1959), are due to Konstantinova, Sylvestrova, Yureen and Aleksandrov, who also proved triglycine sulfate to exhibit memory of the stronger field.

Memory of the stronger AC field as investigated in  $\text{BaTiO}_3$  by Rzhhanov (1949) results from rejuvenation with an AC electric field. Hitherto, ageing in ferroelectric

materials was a process that had been known to take place in systems based on barium titanate.

According to a hypothesis proposed by Pająk and Stankowski (1958), in an ageing ferroelectrics, domains of compensated spontaneous polarisation arise, and fully aged material is probably characterized by antiparallel configuration of the domains. This latter state has been termed domain antiferroelectric. Old samples exhibit a double hysteresis loop — a proof of the presence of the antiferroelectric state. A young sample always presents a normal hysteresis loop, and construction appears in the course of time.

Yureen and Zheludev (1959) proved effects characteristic of ageing to take place in  $\text{CuSO}_4$  doped Rochelle salt. A young sample of Rochelle salt containing an admixture of  $\text{CuSO}_4$  exhibits a normal hysteresis loop which changes to a double loop in the course of 200 hours. The same authors found temperature hysteresis resulting from rejuvenation. Temperature hysteresis had been first observed by Piekara and Pająk (1952) in a system of the  $\text{BaTiO}_3$  type.

#### *Method of measurements*

Triglycine sulfate crystals were grown from the saturated solution by gradually lowering the temperature (from  $36^\circ$  to  $24^\circ\text{C}$ ). Triglycine sulfate with an admixture of  $\text{CuSO}_4$  was obtained by the method of water evaporation at constant temperature ( $+8^\circ\text{C}$ ). The plates were cut perpendicularly to the ferroelectric axis ( $b$ -axis). The hysteresis loops were investigated with the Sawyer-Tower scheme. The dielectric permittivity was measured by the resonance method at a frequency of 1 MHz.

#### *Experimental results*

Immediately following preparation, triglycine sulfate exhibits double and asymmetric hysteresis loops (Fig. 1 a). If an AC electric field is applied to the sample for some minutes, the hysteresis loop is seen to assume the normal shape (Fig. 1 b).



Fig. 1. Oscillograms of hysteresis loops of pure triglycine sulfate: (a) sample immediately after production, (b) sample after some minutes of applying AC field



A more distinct rejuvenating effect of the AC field is shown in Fig. 2. Fig. 2a shows hysteresis loops in triglycine sulfate at a field of  $E = 600$  V/cm. To rejuvenate the sample, and AC field of  $E = 1,600$  V/cm was applied for 5 minutes (Fig. 2b). It is seen that, on reducing the field strength to  $E = 600$  V/cm (Fig. 2c), the polarisation

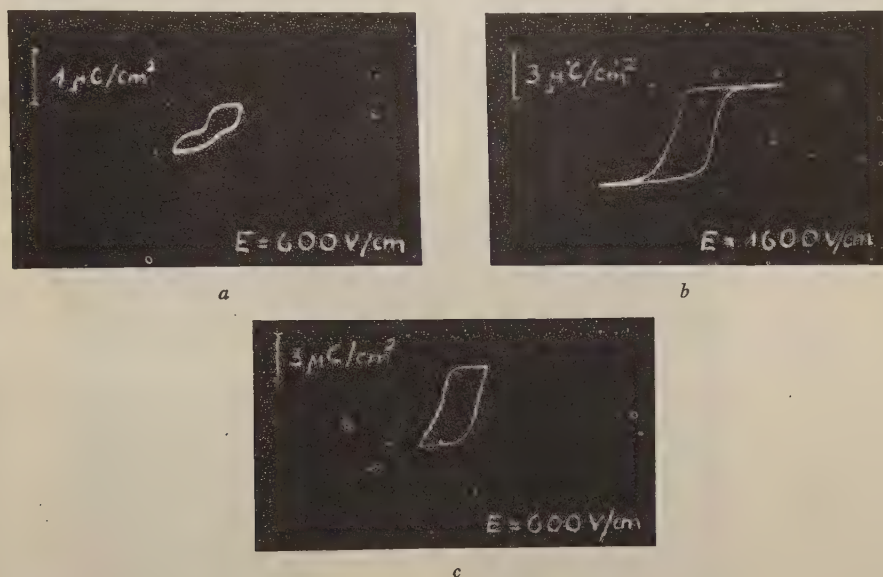


Fig. 2. Oscillograms showing process of rejuvenation: (a) hysteresis loop of old sample,  $E = 600$  V/cm, (b) after 5 minutes of applying a field of  $E = 1600$  V/cm, (c) sample rejuvenated with AC field  $E = 600$  V/cm

and losses for re-polarizing increase considerably. The sample is thus seen to have undergone rejuvenation by the AC field.

By heating the sample above the Curie temperature (e. g. to  $80^\circ\text{C}$ ) and subsequent cooling, a young sample is obtained. The hysteresis loops for a thus rejuvenated sample are shown in Fig. 3a, yielding a polarisation of  $P_s = 2,74 \frac{\mu\text{C}}{\text{cm}^2}$  and a coercive field of  $E_c = 400$  V/cm. In the course of time, the loops become constricted, a symptom that ageing has set in (Fig. 3, b and c).

Almost all samples exhibited asymmetry of the hysteresis loop. This asymmetry is related to the region within the crystal whence the sample had been cut (Fig. 4). The asymmetry of the hysteresis loop does not disappear in the process of rejuvenation. A similar effect has been observed by Holden, Merz, Remeika and Matthias in GASH crystals (1956).

If an admixture of  $\text{CuSO}_4$  is added to triglycine sulfate, a material is obtained that is much less easily rejuvenated in an AC field. On applying a weak field to an old sample, the  $P(E)$  dependence was found to have the shape of a straight line (Fig. 5a).

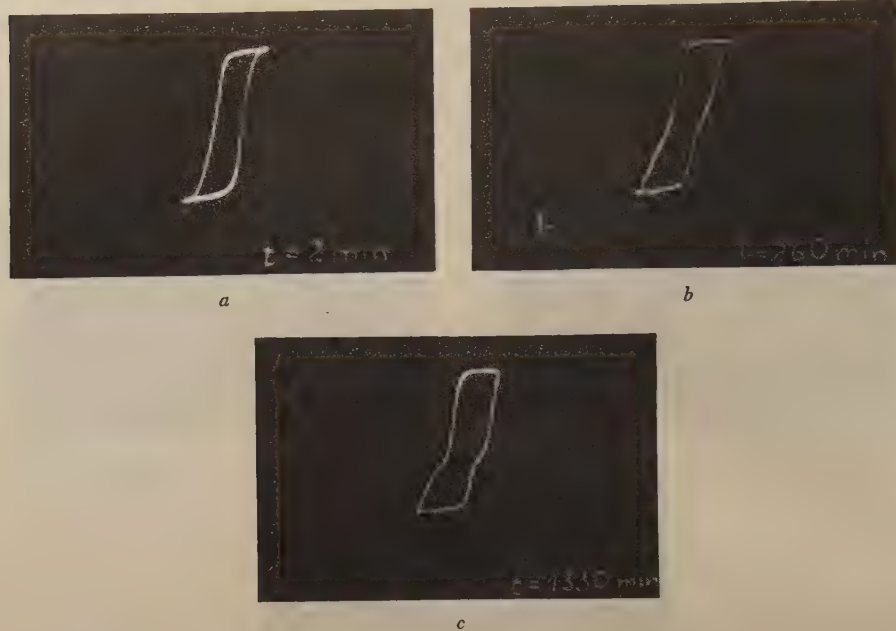


Fig. 3. Oscillograms of the shape of the hysteresis loop as it changes in time, following rejuvenation at 80°C: (a) immediately after rejuvenation, (b) 260 minutes later, (c) 1330 minutes later

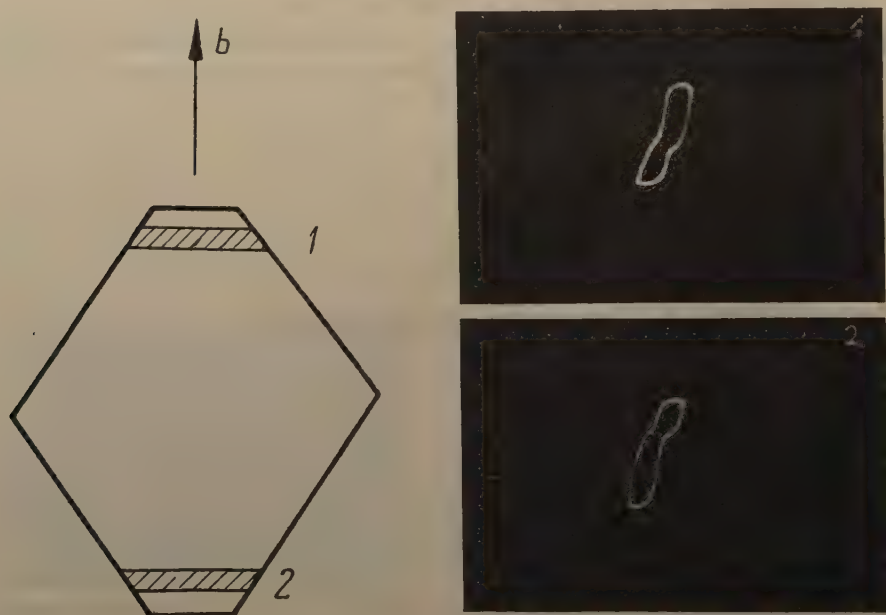


Fig. 4. The asymmetry is related to the region whence the sample is cut. In both cases, the field was applied in the same direction

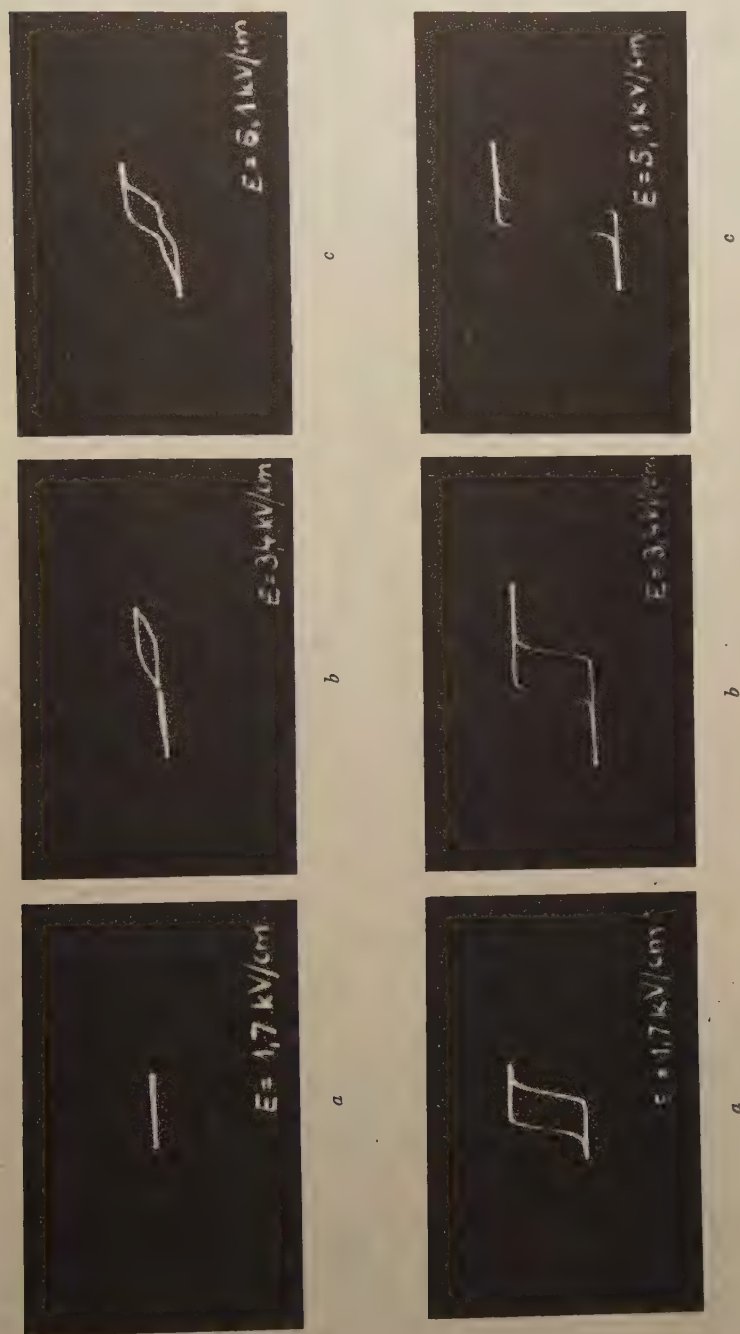


Fig. 5. Oscillograms of the hysteresis loops of a young and an old sample of triglycine sulfate doped with  $\text{CuSO}_4$ , for fields of 1.7, 3.4 and 5.1 kV/cm, respectively

As the field intensity increases, a double loop and, subsequently, a constricted loop is observed (Fig. 5, *b* and *c*). The hysteresis loops obtained at the same field intensities in a sample rejuvenated by heating above the Curie temperature are shown in Fig. 5, *d*, *e* and *f*.

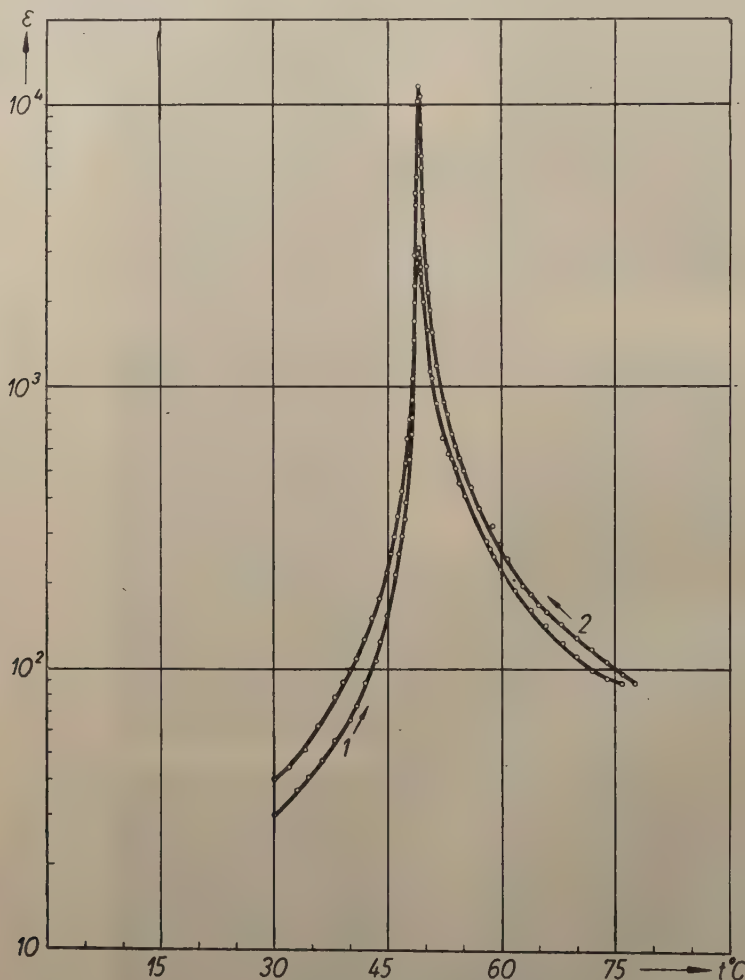


Fig. 6a.  $\varepsilon(T)$  characteristics for sample A

The  $\varepsilon(T)$  dependence will be given here for three samples: *A*) one made of pure triglycine sulfate, *B*) one of triglycine sulfate with a small admixture of  $\text{CuSO}_4$ , grown from a solution containing 0.05%  $\text{CuSO}_4$ , *C*) one prepared from triglycine sulfate with a large admixture of  $\text{CuSO}_4$ , grown a solution containing 0.25%  $\text{CuSO}_4$ .



The  $\varepsilon(T)$  dependence for samples *A*, *B*, *C* is shown in Fig. 6, a, b, c. Curve 1 corresponds to the old sample, whereas curve 2 is that of the young sample. The following table brings the values of the dielectric properties of sample *A*, *B*, *C*:

Sample	$P, \frac{\mu C}{cm^2}$	$E_c, \frac{V}{cm}$	$T_c, ^\circ C$ old sample	$T_c, ^\circ C$ young sample	$\varepsilon$ peak (old)	$\varepsilon$ peak (young)
<i>A</i>	2.74	400	49.2	49.15	3010	11800
<i>B</i>	2.50	650	48.5	48.85	1775	11490
<i>C</i>	0.65	1750	48.2	49.0	148	890

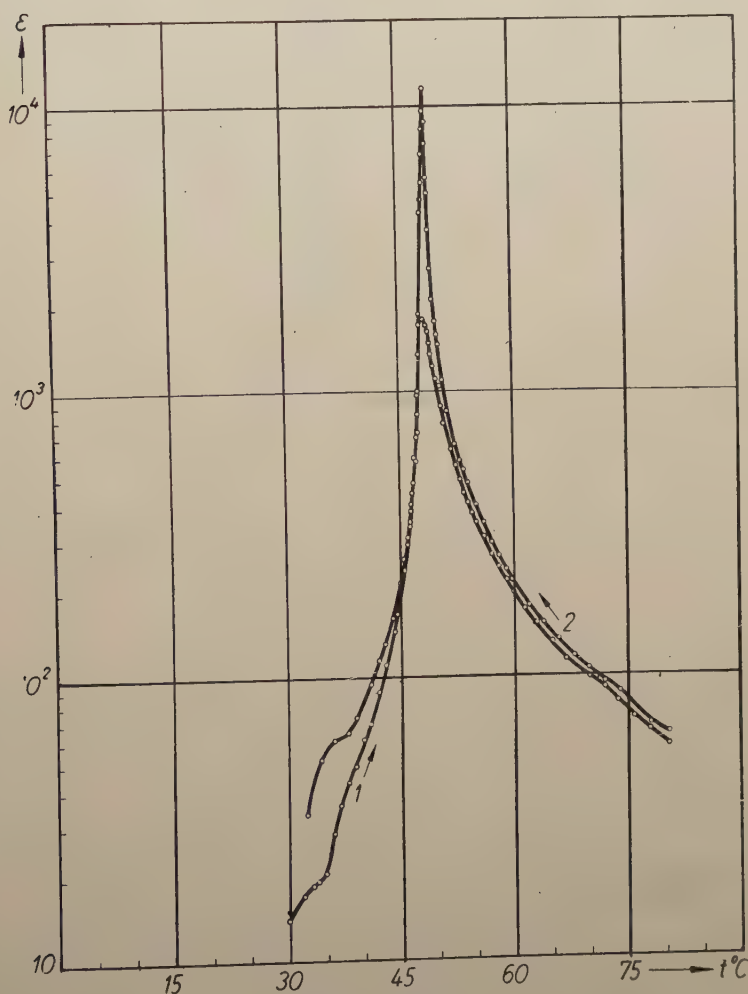


Fig. 6 b.  $\varepsilon(T)$  characteristics for sample *B*.

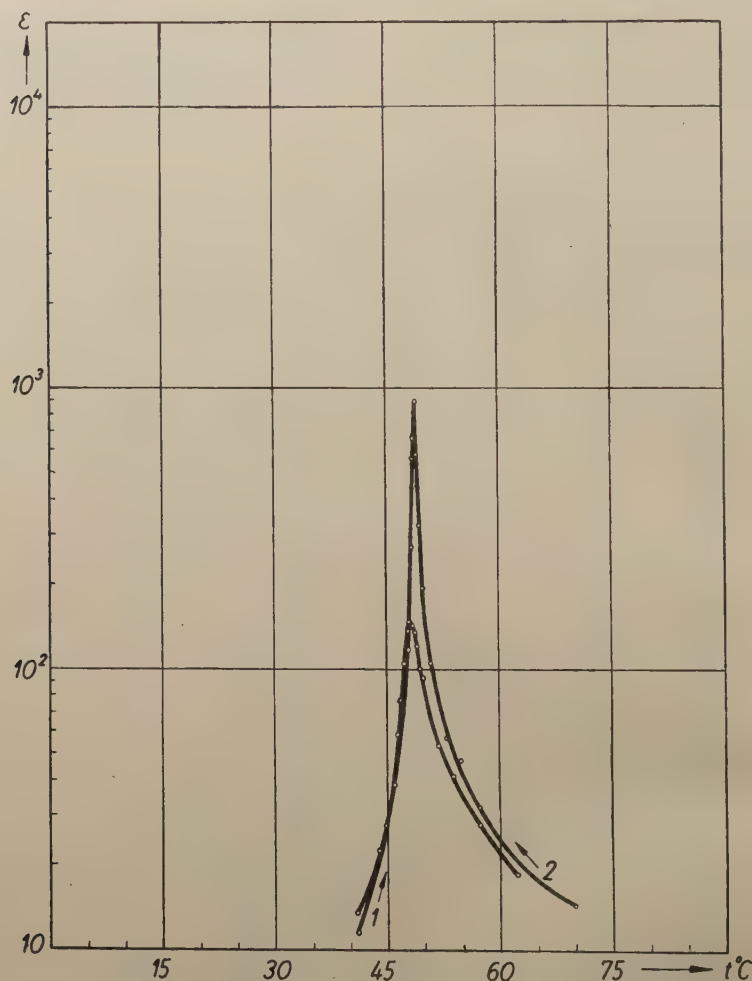


Fig. 6c.  $\varepsilon(T)$  characteristics sample C.

The measurements of  $P_s$  and  $E_c$  were carried out at 20°C for young samples.

### Discussion

The results of the present investigation can be summed up as follows:

1. Triglycine sulphate undergoes ageing, since young material exhibits a normal hysteresis loop that becomes constricted in the course of time.
2. Admixtures have the effect of fixing the domain antiferroelectric state, as in the cases of  $\text{BaTiO}_3$  (Pajak, Stankowski 1958) and Rochelle salt (Yureen, Zheludev 1959).
3. A larger admixture lowers the Curie temperature  $T_c$  of and old sample; the peak value of  $\varepsilon$  decreases, and so does that of  $P_s$ , whereas the coercive field  $E_c$  increases.

4. The asymmetry and electric properties depend on the region in the crystal at which the sample had been cut out.

5. Temperature hysteresis in triglycine sulfate is somewhat different in shape from that occurring in doped  $\text{BaTiO}_3$  (Piekara, Pająk 1952), and Rochelle salt (Yureen, Zheludev 1959), where a young sample exhibits a lower  $T_c$  value than an old one (Yureen, Zheludev 1959), (Pająk 1957).

6. In  $\text{CuSO}_4$  doped triglycine sulfate,  $T_c$  in the young sample is displaced towards higher temperatures, inversely as in  $\text{BaTiO}_3$  and Rochelle salt. The value of  $\epsilon$  at the Curie point exhibited by a young sample exceeds the respective value for an old one. A similar effect has been observed in doped  $\text{BaTiO}_3$  (Piekara, Pająk 1952) and Rochelle salt (Yureen, Zheludev 1959).

It seems that all old ferroelectrics present the domain antiferroelectric state. Admixtures tend to fix this state. This is best seen in Rochelle salt. The latter presents antiparallel domain configuration; however, because of the low activation energy for reorientation, no double hysteresis loops are observed. Admixtures raise the activation energy. On the other hand, an admixture homogeneously distributed throughout the material produces an increase in the coercive field, and does not lead to the appearance of a double hysteresis loop. A young doped ferroelectric presents the usual hysteresis loop. It is only in the process of ageing that admixtures have the effect of fixing the domain antiferroelectric state. Some kind of specific ordering of the defects occurs here. It would seem that diffusion of the defects towards the walls separating the domains increases the activation energy for reorientation. This, probably, constitutes the microscopic mechanism of the process of ageing in doped crystals. In pure crystals, however, the ageing process, though not so pronounced, seems to be due to minor amounts of impurities or defects diffusing towards the domain walls.

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## ENERGY SPECTRA OF CHARGED PIONS PRODUCED IN $pd$ -COLLISIONS AT 660 MeV\*

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The energy spectra of charged pions produced in  $pd$ - and  $pp$ -collisions has been measured using a magnetic spectrometer. The differential cross sections for the  $p + d \rightarrow \pi^+$ ,  $p + d \rightarrow \pi^-$ , and  $p + p \rightarrow \pi^+$  processes at  $90^\circ$  in the center of mass system of two colliding nucleons were found to be  $(5.0 \pm 0.6) \times 10^{-28}$ ,  $(0.57 \pm 0.08) \times 10^{-28}$  and  $(6.7 \pm 0.7) \times 10^{-28}$  cm<sup>2</sup>/sterad, respectively. The ratio of the efficiency of positive pion productions on protons in deuterons and on free protons is equal to  $0.79 \pm 0.08$ .

### I. Introduction

From the experimental data obtained at 460 and 660 MeV<sup>1,2)</sup> and at 970 MeV<sup>3)</sup> it follows that the proton-deuteron collisions without pion production are, mainly, a quasi-elastic scattering of incident protons by single nucleons in deuterons similar in general to the scattering of protons by free nucleons. Only in rare cases the incident protons interact simultaneously with both nucleons inside a deuteron. Such triple collisions involve also the elastic  $pd$ -scattering whose differential cross section at the energies 460 and 660 MeV and in the region of large scattering angles is equal to  $\sim 10^{-29}$  cm<sup>2</sup>/sterad. Due to a proton-nucleon character of the high energy  $pd$ -collisions the possible reactions of a single pion production are

$$p + p + (n) \rightarrow \pi^+ + p + n + (n), \quad (1)$$

$$p + p + (n) \rightarrow \pi^0 + p + p + (n), \quad (2)$$

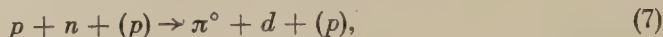
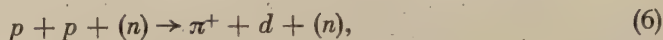
$$p + n + (p) \rightarrow \pi^+ + n + n + (p), \quad (3)$$

$$p + n + (p) \rightarrow \pi^0 + p + n + (p), \quad (4)$$

$$p + n + (p) \rightarrow \pi^- + p + p + (p), \quad (5)$$

\* Reported at the 6th Session of the Scientific Council of the Joint Institute for Nuclear Research, June 1, 1959.

where (*n*) and (*p*) denote nucleons not colliding directly with incident protons, and therefore emitted with low energy. According to Batson et al.<sup>3)</sup> the probable energy of non-colliding protons in *pd*-collisions at 970 MeV is about 5 MeV, their angular distribution being weakly correlated with the direction of the incident beam. In *pd*-collisions the production of pions is possible also in reactions in which two or three nucleons in final state are bound. These reactions can be as follows:



In the experiments described the production of charged pions in *pd*-collisions. was studied by measuring the energy spectra of positive pions from the reactions (1), (3), (6) and of negative pions from the reaction (5). The peak was also searched which would correspond to positive pions from the reaction (8). Besides, under conditions strictly identical to those of the observation of pions from *pd*-collisions, the energy spectrum of positive pions produced in free *pp*-collisions was measured. Such comparative study of high-energy *pd*- and *pp*-collisions can give informations on the effect of nuclear binding of nucleons in a deuteron on the process of pion production.

## 2. Experimental Methods

The present experiments were carried out with the six-meter synchrocyclotron of the Joint Institute for Nuclear Research. Use was made of the external unpolarized proton beam focussed by quadrupole lenses and passed through a deflecting magnet. Near the target, a thin-wall cylindrical container 4 cm in diameter and 12 cm high, filled with either liquid hydrogen or liquid deuterium, the proton density in the beam  $2 \times 3$  cm cross section was  $\sim 2.10^8$  protons/cm<sup>2</sup> sec. The container was placed into a vacuum chamber cooled with liquid hydrogen. The external casing of the chamber was cooled with liquid nitrogen. It was supposed that the liquid deuterium and liquid hydrogen in the container were kept at the temperature of boiling hydrogen; their densities were equal to 0.169 and 0.0708 g/cm<sup>3</sup>, respectively<sup>4)</sup>. The effect of empty container was smaller than 3% of the particle emission in presence of liquid hydrogen or liquid deuterium. The proton energy in the center of the target was equal to  $(654 \pm 5)$  MeV.

The energy spectra of pions were measured by means of a magnetic spectrometer previously described by Azhgirei et al.<sup>5)</sup> Fig. 1 gives the schematic diagram of the spectrometer and its location with respect to the proton beam. In our experiments as well as in 5) two thin scintillation counters  $C_1$  and  $C_2$  placed at the input of the spectrometer separated a particle beam emitted at the angle of  $56^\circ$  to the direction of the primary proton beam. This angle of emission of positive pions from the reaction

$p + p \rightarrow \pi^+ + d$  corresponds to the angle of  $90^\circ$  in the center of mass system (c. m. s.) of the two colliding protons. The analysed beam on the horizontal plane was about  $\pm 2^\circ$ . The particles passed through channel II of the spectrometer were detected by a telescope consisting of four scintillation counters. The relative width  $\Delta p/p$  of the momentum interval selected by the scintillators was about  $\pm 3\%$  for all measured

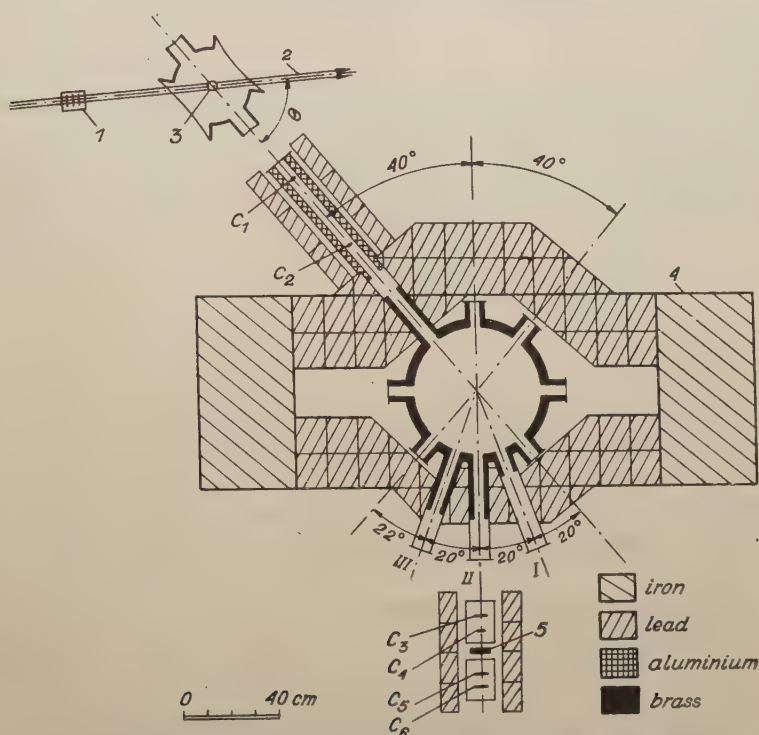


Fig. 1. Experimental arrangement. 1. Monitor. 2. Proton beam. 3. Target. 4. Magnet. 5. Filter.  $C_1, \dots, C_6$  scintillators.

momenta, the subtended solid angle being about  $0.5 \times 10^{-4}$  sterad. The threshold of pion detection was at 35 MeV. The dependence of a mean momentum of particles passing through the spectrometer from the magnet current was determined by current-carrying wire techniques.

In the runs of the experiments the six-fold coincidences of pulses from the counters at the input and output of the spectrometer were detected simultaneously with four-fold coincidences from the counters of only one output telescope. The background of accidental coincidences was found by switching on the delay lines shifting the pulses from separate pairs of counters  $C_1 C_2$ ,  $C_3 C_4$  and  $C_5 C_6$ . In choosing the delay value the fine time structure of the synchrocyclotron proton beam was taken into account. The detection efficiency of scintillations was close to 100% in all investigated energy regions. The small contamination of secondary protons was separated

from pions by means of a filter placed in front of the next to last scintillator of the output telescope. The relative contamination of  $\mu$ -mesons and electrons in the particle beam passed through the spectrometer was determined by means of measuring the range curves in copper. To the results of measurements corrections were introduced which took into account decay in flight of pions as well as their slowing down and absorption in the target, scintillators and in the filter separating the secondary protons from mesons.

The absolute values of differential cross sections in spectra,  $d^2\sigma/d\Omega \cdot dE$ , were estimated with the accuracy of about 7% by comparing yields of positive and negative pions with that of recoil protons from the elastic  $pp$ -scattering. For 655 MeV at  $56^\circ$  in the lab. system ( $120^\circ$  in c. m. s.), the differential cross section of the elastic  $pp$ -scattering was taken equal to  $(6.7 \pm 0.26) \times 10^{-27} \text{ cm}^2/\text{sterad}$  (in c. m. s.  $(3.41 \pm 0.13) \times 10^{-27} \text{ cm}^2/\text{sterad}$ )<sup>6</sup>.

### 3. Results of Measurements and Discussion

The energy spectra of charged pions obtained from  $pd$ -collisions are given in Fig. 2 and 3 together with the statistical errors of measurements. For comparison in fig. 2 the spectrum of positive pions from free  $pp$ -collisions is plotted with a solid line without indicating the experimental points. This spectrum is measured with the same accuracy as the spectrum of positive pions from  $pd$ -collisions. All the rest of the errors connected with the determination of absolute values  $d^2\sigma/d\Omega \cdot dE$  and with

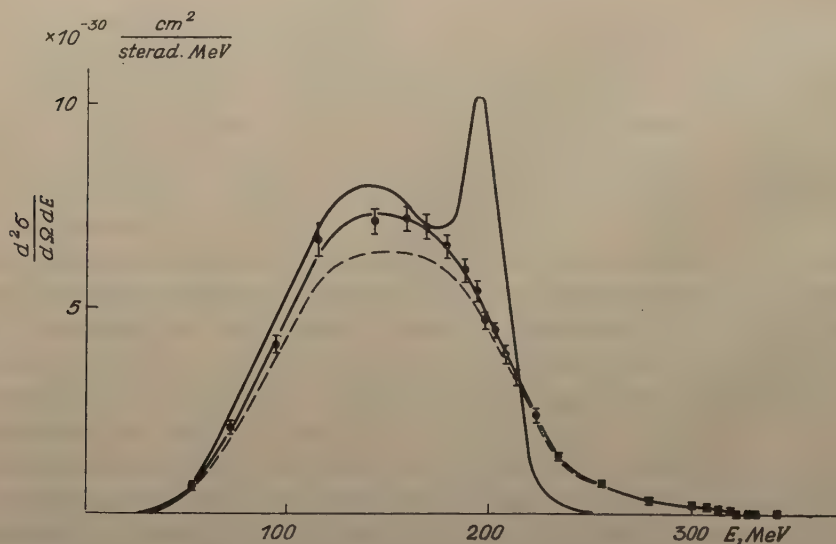


Fig. 2. Energy spectra of positive pions in the lab. system. The upper curve corresponds to free  $pp$ -collisions; the curve plotted according to experimental points corresponds to  $pd$ -collisions; the dashed line — to  $pp$ -collisions in deuterons.



the estimation of corrections introduced were taken into account in calculating the differential cross sections  $d\sigma/d\Omega$  of the observed reactions. Below 70 MeV the validity of experimental data on the form of spectra is not high, due to great difficulties with which the determination of  $\mu$ -meson contamination in this energy region is connected. The usual transformation of the spectra to the c. m. s. showed that in this system the angles of emission of a great part of the pions lie in the range of  $90^\circ$ — $97^\circ$ .

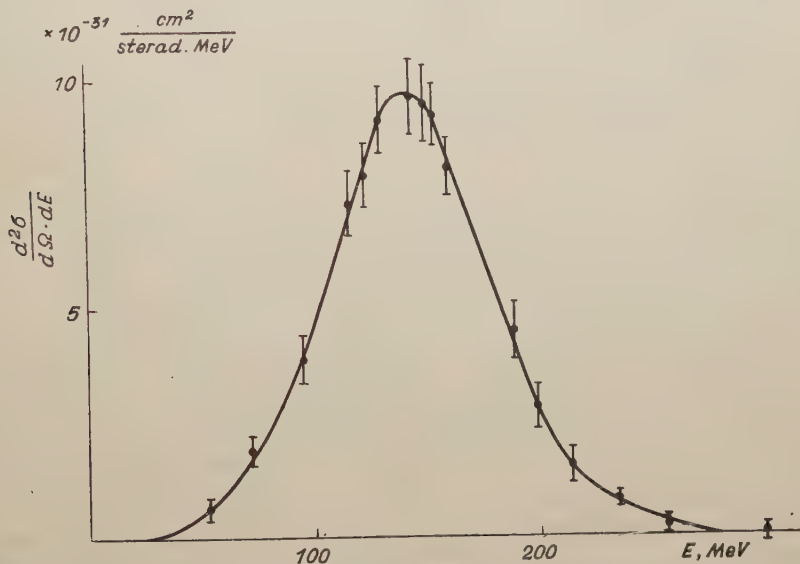


Fig. 3. Energy spectrum of negative pions from  $pn$ -collisions in deuterons.

When double pion production in one nucleon-nucleon interaction is rare, it is sufficient to consider that negative pion production by protons on deuterons as occurring only in  $pn$ -collisions, while positive mesons are produced both in  $pp$ - and  $pn$ -collisions. Due to charge symmetry, the differential cross sections for the reactions  $p + n \rightarrow \pi^+ + n + n$  and  $p + n \rightarrow \pi^- + p + p$  are connected by the relation

$$\frac{d\sigma}{d\Omega} (p + n \rightarrow \pi^+ + n + n)_{\vartheta} = \frac{d\sigma}{d\Omega} (p + n \rightarrow \pi^- + p + p)_{180^\circ - \vartheta},$$

where  $\vartheta$  is the angle of the pion emission in the c. m. s. At  $\vartheta = 90^\circ$  the differential cross sections of the above reactions must be equal to each other, and the spectra of positive and negative mesons must be of the same form. Taking into account this inference from charge symmetry, one can expect that the result of subtraction of the spectrum of negative pions produced in the reaction (5) from the observed total spectrum of positive pions of the reactions (1), (3) and (6) is the spectrum of positive pions only from  $pp$ -collisions in deuterons. The spectrum of positive pions thus obtained and plotted in Fig. 2 with a dashed line spreads towards high energies farther

than the spectrum of positive pions from free  $pp$ -collisions. This, apparently, is due to the motion of protons in deuterons. The absence of a peak from the reaction  $p + p \rightarrow \pi^+ + d$  in the spectrum of positive pions from  $pp$ -collisions in deuterons, distinctly observed at 196 MeV in the case of free  $pp$ -collisions can be explained in the same manner. Nevertheless, if one normalizes the spectra of positive pions produced on protons in deuterons and in free protons to equal areas, and then subtracts the contribution of the reaction  $p + p \rightarrow \pi^+ + d$  from the spectrum of positive pions produced in free  $pp$ -collisions, it turns out that in the region of the peak corresponding to the reaction  $p + p \rightarrow \pi^+ + d$  the values  $d^2 \sigma / d\Omega dE (p + p^+ \rightarrow \pi^+ + \dots)_D$  exceed the values  $d^2 \sigma / d\Omega dE (p + p \rightarrow \pi^+ + n + p)_H$ . This fact indicates that in  $pd$ -collisions the reaction (6) is still contributing to the yield of positive pions.

The absence of a peak corresponding to the reaction (8) in the spectrum of positive pions from  $pd$ -collisions is not a surprise as already at 340 MeV<sup>7)</sup> the total cross section of this reaction is about  $10^{-29}$  cm<sup>2</sup>. From the positive pion yield near the upper limit of the spectrum ( $E_\pi = 310$  MeV) where the peak of positive pions from the reaction (8) would be observed, one can conclude that if at 660 MeV the reaction (8) occurs its differential cross section for positive pion emission in the direction of 56° to the proton beam does not exceed  $\sim 5 \cdot 10^{-30}$  cm<sup>2</sup>/sterad.

Comparing the spectra of positive and negative pions produced in  $pp$ - and  $pn$ -collisions in deuterons can see that to the right from the maximum the spectrum of negative pions falls more rapidly than that of positive pions. This difference, exceeding the limits of experimental errors, can be explained by the fact that in the reactions  $p + p \rightarrow \pi^+ + n + p$  and  $p + n \rightarrow \pi^- + p + p$  the effect of nucleon-nucleon interaction in a final state is not the same. Indeed, in the first reaction the transition of  $T = 1 \rightarrow T = 0$  of the initial and final isotopic spin states of the two-nucleon system leaves the neutron and the proton in  $^3S$ -state. Due to a strong interaction between nucleons in this state, the nucleons are emitted predominantly with low energies of relative motion and thus the energy taken by the pion increases. On the contrary, in the reaction  $p + n \rightarrow \pi^- + p + p$  the transition  $T = 1 \rightarrow T = 1$  takes a considerable part which leaves the protons in  $^3P$  state when the interaction between them is weak.

The maxima of all the spectra (for  $pp$ -collisions only continuous spectrum from the reaction  $p + p \rightarrow \pi^+ + n + p$  is taken into account) are found practically at one energy, as is seen from the table in which the values of the mean meson energy in the spectra are also given. As it should be expected, the obtained meson spectra differ in form from that calculated with taking into account of only one statistical weight of the final states. It is essential that the maxima in the spectra transformed to the c. m. s. are detected in the energy region closely corresponding to the energy of the maximum of  $\pi^+ + p$ -scattering cross section in the  $\pi^+ - p$  c.m. system. This fact indicates that in the processes of pion production in  $pd$ -collisions the resonance interaction between a pion and a nucleon in the state with  $J = T = 3/2$  plays an important role.

Reaction	Energy of the maximum (lab. s.) MeV	Energy of the maximum (c.m.s.) MeV	Mean energy of meson (lab. s.) MeV	Mean energy of meson (c.m. s.) MeV
$p + p \rightarrow \pi^+ + p + n$	$142 \pm 5$	$106 \pm 5$	—	—
$p + d \rightarrow \pi^+ + \text{nucl.}$	$145 \pm 8$	$109 \pm 8$	151	116
$p + d \rightarrow \pi^- + \text{nucl.}$	$143 \pm 5$	$107 \pm 5$	144	108

Integrating the spectra in the c. m. s. over the energy, the following values of the differential cross sections of the observed reactions were obtained:

$$\frac{d\sigma}{d\Omega} (p + p \rightarrow \pi^+ + \dots) = (6.7 \pm 0.7) \times 10^{-28} \text{ cm}^2/\text{sterad},$$

$$\frac{d\sigma}{d\Omega} (p + d \rightarrow \pi^+ + \dots) = (5.9 \pm 0.6) \times 10^{-28} \text{ cm}^2/\text{sterad},$$

$$\frac{d\sigma}{d\Omega} (p + d \rightarrow \pi^- + \dots) = (0.57 \pm 0.08) \times 10^{-28} \text{ cm}^2/\text{sterad}$$

The differential cross section for positive pion production in free  $pp$ -collisions at 660 MeV at  $90^\circ$  in the c. m. s. is close to the value  $(6.8 \pm 1.5) \times 10^{-28} \text{ cm}^2/\text{sterad}$  obtained by Neganov and Savchenko<sup>8)</sup> but distinctly smaller than the value  $(9.3 \pm \pm 0.7) \times 10^{-28} \text{ cm}^2/\text{sterad}$  reported by Meshkovsky at al<sup>9)</sup>.

The cross section  $\frac{d\sigma}{d\Omega} (p + p \rightarrow \pi^+ + \dots)_D = \frac{d\sigma}{d\Omega} (p + d \rightarrow \pi^+ + \dots) - \frac{d\sigma}{d\Omega} (p + d \rightarrow \pi^- + \dots) = (5.3 \pm 0.7) \times 10^{-28} \text{ cm}^2/\text{sterad}$  corresponds to the integral yield of positive pions from the reactions (1) and (6). The ratio of probabilities of positive meson production in collisions of protons with free and bound protons is equal to

$$\frac{\frac{d\sigma}{d\Omega} (p + p \rightarrow \pi^+ + \dots)_D}{\frac{d\sigma}{d\Omega} (p + p \rightarrow \pi^+ + \dots)_H} = 0.79 \pm 0.08$$

As the spectra of pions from  $pd$ - and  $pp$ -collisions are measured in strictly identical conditions, the accuracy of determination of the value of this ratio is due only to statistical errors of measurements of pion yields and  $\mu$ -meson contamination.

The fact that in case of pion production the protons in deuterons are less effective than the free protons is due to: (i) intranuclear motion of nucleons and their mutual "eclipses" in deuterons<sup>\*\*</sup>; (ii) higher reabsorption of mesons by recoil nucleons in

<sup>\*\*</sup> According to Prokoshkin's estimation (private communication) at the energy 660 MeV as a result of intranuclear motion the cross sections for meson production in nucleon-nucleon collisions in deuterons must be about 4% smaller as compared to those on free nucleons.

case of  $pd$ -collisions; (iii) the effect of exclusion principle for recoil nucleons in  $pd$ -collisions. The ratio

$$\frac{d\sigma}{d\Omega}(p + p \rightarrow \pi^+ + \dots)_D \bigg/ \frac{d\sigma}{d\Omega}(p + p \rightarrow \pi^+ + \dots)_H$$

can in general differ from unity if only in processes  $(p + p \rightarrow \pi + \dots)_D$  and  $(p + p \rightarrow \pi^+ + \dots)_H$  the interference between amplitudes of possible meson-nucleon states is different. From the data obtained it follows that at  $90^\circ$  in the c. m. s. the relation of the number of positive pions to that of negative ones from deuterium is equal to  $10.3 \pm 1.3$ . If in nucleon-nucleon collisions pions were produced only through the resonant state ( $J = T = 3/2$ ), the ratio of total cross sections of positive and negative pion-production for  $pd$ -collisions would be equal to  $11^{(10)}$ .

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# RANDWERTPROBLEME IM GEBIETE DER DURCH ELEMENTARGESETZE DEFINIERTEN LINEAREN SKALARFELDER IN ISOTROPEN UND HOMOGENEN RÄUMEN

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In der vorliegenden Note wird als das lineare Skalarfeld, das durch das Elementargesetz  $\varphi = \varphi(r)$  definiert ist, das Feld

$$F(x, y, z) = \sum_{a, b, c=0}^{\infty} A_{abc} \frac{\partial^l \varphi(r)}{\partial x^a \partial y^b \partial z^c} \quad (l = a + b + c)$$

angesehen, wobei die Koeffizienten  $A_{abc}$  beliebige komplexe Zahlen sein können. Es wird für solche Felder die Lösbarkeit von Randwertaufgaben untersucht, die durch die Vorgabe der Werte für

$$F, \frac{\partial F}{\partial N}, \frac{\partial^2 F}{\partial N^2}, \dots, \frac{\partial^{n-1} F}{\partial N^{n-1}}$$

an der Begrenzungsfläche des Raumes definiert sind, in dem das Randwertproblem vorgegeben ist. Es wird bewiesen, daß ein solches Randwertproblem für endliche  $n$ -Werte nur in dem Falle gelöst werden kann, falls das Elementargesetz  $\varphi = \varphi(r)$  und daher auch das Feld  $F(x, y, z)$  Lösungen einer partiellen Differentialgleichung von der Gestalt

$$\sum_{i=0}^n a_i \Delta^i F(x, y, z) = 0 \quad (a_n \neq 0)$$

sind.

## § 1. Definition von linearen Skalarfeldern, die durch Elementargesetze erzeugt werden

In den Zeiten als die Physiker noch nicht davon träumten, die Gesetze der Feldphysik durch partielle Differentialgleichungen darzustellen, da ja doch diese damals noch unbekannt waren, bediente man sich der Elementargesetze zur Darstellung

des Naturgeschehens. Es sei etwa an das Newtonsche Elementargesetz der Gravitation erinnert.

Die Gesetze der Felder, denen wir in der modernen Physik begegnen, werden hingegen fast ausschließlich mit Hilfe von partiellen Differentialgleichungen festgelegt. Im Falle daß diese Differentialgleichungen linear sind, ergeben sich aus ihnen, je nach ihrer Ordnung, ein oder mehrere Elementargesetze, die gewöhnlich als die Grund- oder Fundamentallösungen bezeichnet werden. Auf diese Weise ist es stets möglich die Lösungen der linearen Feldgleichungen mit Hilfe von Elementargesetzen darzustellen. Diese Möglichkeit besteht nicht nur im Falle der Felder, die durch partielle Differentialgleichungen vom elliptischen Typus beherrscht werden, sondern auch im Falle von hyperbolischen Differentialgleichungen. Auf diese Weise kehren wir im Falle linearer Felder eigentlich zum Standpunkte der Elementargesetze zurück.

Wie aus einer früheren Arbeit des Verfassers (Rubinowicz 1951, wird im folgenden als A zitiert) und den nachfolgenden Überlegungen hervorgeht, sind jedoch die mit Hilfe der Elementargesetze definierten linearen Felder allgemeiner als die durch partielle Differentialgleichungen darstellbaren. Angesichts der Schwierigkeiten, denen man heute in der Feldphysik begegnet, ist es deshalb vielleicht von Interesse die Frage zu stellen, wodurch die linearen Felder, die durch partielle Differentialgleichungen definiert werden können, sich gegenüber den nur durch Elementargesetze angebbaren auszeichnen.

Wie man auf Grund von Elementargesetzen lineare Felder in einem isotropen und homogenen Raume festlegen kann, wurde in A für den Fall von skalaren Feldern gezeigt. Als das zum Elementargesetz  $\varphi = \varphi(r)$  gehörige<sup>1</sup> in dem Quellpunkte  $Q$  (je nach dem Elementargesetz) reguläre oder hier auch Singularitäten aufweisende Feld haben wir das durch

$$F(x, y, z) = \sum_{a,b,c=0}^{\infty} A_{abc} \frac{\partial^l \varphi(r)}{\partial x^a \partial y^b \partial z^c} \quad (l = a + b + c) \quad (1.1)$$

gegebene Feld anzusehen. Die Koeffizienten  $A_{abc}$  sind hier komplexe Zahlen deren Wahl nur durch die Forderung eingeschränkt wird, daß (1.1) konvergiert. Die einzelnen in der Summe (1.1) auftretenden Ableitungen wollen wir nun als Felder von Gegenüberstellungsmultipolen<sup>2</sup> bezeichnen, weil man sie im Sinne der Maxwellschen Konstruktion von Multipolfeldern interpretieren kann. Da man das Quellsystem eines durch eine Ableitung  $l$ -ter Ordnung gegebenen Feldes als aus  $2^l$  einfachen Quellpunkten bestehend ansehen kann, soll es das Quellsystem eines Gegenüberstellungsmultipols  $2^l$ -ter Ordnung heißen.

<sup>1</sup> Das Elementargesetz  $\varphi = \varphi(r)$  kann auch von der Zeit abhängen, also z. B. eine Kugelwelle  $f(r-ct)/r$  darstellen, die einem beliebigen Zeitgesetze entspricht (vgl. A, § 7).

<sup>2</sup> In A wurden sie Felder mehrfacher Quellen genannt.

Außerdem haben wir in A den Begriff von Feldern eingeführt, die wir nun als Felder von Kugelfunktionenmultipolen<sup>3</sup> bezeichnen wollen. Sie sind als die Felder (1.1) definiert, die sich in der Gestalt

$$Y_{lm}(\vartheta, \varphi) R_l^{l+2s}(r) \quad (1.2)$$

darstellen lassen. Ein Feld (1.2) das eine Kugelfunktion  $Y_{lm}(\vartheta, \varphi)$   $l$ -ter Ordnung enthält, soll ein Feld eines Kugelfunktionenmultipols  $2^l$ -ter Ordnung heißen.

Um ein solches Feld aus Feldern von Gegenüberstellungsmultipolen aufzubauen, hat man sich eines Operators  $Y_{lm} \left( \frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right)$  zu bedienen, der in der nachstehenden Weise hergestellt werden kann: Bezeichnen wir mit  $Y_{lm}(x, y, z)$  die in kartesischen Koordinaten dargestellte räumliche Kugelfunktion, die der flächenhaften Kugelfunktion  $Y_{lm}(\vartheta, \varphi)$  entspricht. Es ist also

$$Y_{lm}(x, y, z) = r^l Y_{lm}(\vartheta, \varphi). \quad (1.3)$$

Bekanntlich ist (1.3) ein in  $x, y, z$  homogener Ausdruck  $l$ -ten Grades, der der Potentialgleichung  $\Delta Y_{lm}(x, y, z) = 0$  genügt. Der gesuchte Operator wird dann erhalten, wenn man in  $Y_{lm}(x, y, z)$  die Koordinaten  $x, y, z$  durch die Differentiationsoperatoren  $\partial/\partial x, \partial/\partial y, \partial/\partial z$  ersetzt. Wie man etwa mit Hilfe gruppentheoretischer Methoden beweisen kann, (vgl. A), besteht dann die Beziehung

$$Y_{lm} \left( \frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right) \Delta^s \varphi(r) = Y_{lm}(\vartheta, \varphi) R_l^{l+2s}(r), \quad \text{wo} \quad (1.4)$$

$$R_l^{l+2s}(r) = r^l \left( \frac{1}{r} \frac{d}{dr} \right)^l \Delta^s \varphi(r) = r^l \left( \frac{1}{r} \frac{d}{dr} \right)^l \left( \frac{1}{r^2} \frac{d}{dr} r^2 \frac{d}{dr} \right)^s \varphi(r). \quad (1.5)$$

In der von uns benutzten Terminologie stellt die rechte Seite der Beziehung (1.4) das Feld eines Kugelfunktionenmultipols  $2^l$ -ter Ordnung dar, dessen Richtungsabhängigkeit durch die Kugelfunktion  $Y_{lm}(\vartheta, \varphi)$  bestimmt wird. Gemäß der linken Seite von (1.4) kann dieses Feld durch eine Summe von Feldern von Gegenüberstellungsmultipolen von der Ordnung  $2^{l+2s}$  dargestellt werden. Bei beliebig vorgegebenem Elementargesetz  $\varphi = \varphi(r)$  gibt es somit verschiedene Felder von Kugelfunktionenmultipolen  $2^l$ -ter Ordnung mit einer gegebenen Kugelfunktion  $Y_{lm}(\vartheta, \varphi)$  je nachdem sie durch Felder von Gegenüberstellungsmultipolen der gleichen sowie der beliebig höheren Ordnungen  $2^{l+2}, 2^{l+4}, 2^{l+6}, \dots$  dargestellt werden. Sie unterscheiden sich selbstverständlich durch die Radialfunktionen  $R_l^{l+2s}(r)$  (1.5).

In A wurden nun die Konsequenzen der Forderung untersucht, daß die Anzahl der linear unabhängigen Gegenüberstellungsmultipolfelder, die zu einem gegebenen Elementargesetz  $\varphi = \varphi(r)$  und einer bestimmten Kugelfunktion  $l$ -ter Ordnung  $Y_{lm}(\vartheta, \varphi)$  gehören, nicht größer sein solle als  $n$ . Es wurde gezeigt, daß in diesem Falle

<sup>3</sup> In A hießen sie einfach Multipolfelder.

das Elementargesetz  $\varphi = \varphi(r)$  und daher auch das mit seiner Hilfe aufgebaute Feld (1.1) Lösungen einer partiellen Differentialgleichung von der Gestalt

$$\sum_{i=0}^n a_i \Delta^i F(x, y, z) = 0 \quad (1.6)$$

sein müssen.

Wir sehen somit: Stellt man an ein lineares, in einem isotropen und homogenen Raume definiertes Skalarfeld (1.1) die Forderung, daß die Anzahl der Felder von Kugelfunktionenmultipolen mit einer bestimmten Kugelfunktion  $Y_{lm}(\vartheta, \varphi)$  die Zahl  $n$  nicht überschreitet, so müssen diese Felder der partiellen Differentialgleichung (1.6) genügen. Die Gleichung (1.6) ist somit die allgemeinste partielle Differentialgleichung in einem isotropen und homogenen Raume, der ein lineares Skalarfeld genügen muß, damit es nur eine endliche Anzahl, nämlich höchstens  $n$  Felder von der Gestalt (1.2) gibt, die eine bestimmte Kugelfunktion  $Y_{lm}(\vartheta, \varphi)$  enthalten und einem bestimmten Elementargesetz entsprechen.

Wie in A gezeigt wurde, kann das Feld  $F(x, y, z)$  (1.1) statt durch Gegenüberstellungsmultipole auch durch Kugelfunktionenmultipole dargestellt werden. Es wird dann durch

$$F(r, \vartheta, \varphi) = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} Y_{lm}(\vartheta, \varphi) \sum_{s=0}^{\infty} c_{lm}^s R_l^{l+2s}(r) \quad (1.7)$$

gegeben.

Wird das Feld  $F(x, y, z)$  durch eine Lösung einer Differentialgleichung vom Typus (1.6) gegeben, so kann es, wie in A ausgeführt und bereits oben bemerkt wurde, je nach der Ordnung dieser Differentialgleichung im allgemeinen nur mit Hilfe mehrerer Elementargesetze beschrieben werden. Schon im Falle der Wellengleichung  $\Delta u + k^2 u = 0$  muß man etwa die beiden Elementargesetze  $e^{ikr}/r$  und  $\sin kr/r$  verwenden, um nicht nur im Quellpunkte singuläre, sondern auch hier reguläre Lösungen zu erhalten. Im Falle der Differentialgleichung (1.6) von der Gestalt  $(\Delta + k^2)(\Delta - \kappa^2)u = 0$  ist man überdies gezwungen auch noch etwa die beiden Elementargesetze  $e^{+kr}/r$  und  $e^{-kr}/r$  zu benützen.

Im Falle von Feldern  $F(x, y, z)$ , die durch Differentialgleichungen (1.6) gegeben werden, treten, wie in A gezeigt wurde, in manchen Fällen auch Felder von Kugelfunktionenmultipolen von der Gestalt  $Y_{lm}(\vartheta, \varphi) S_l^{l+2s}(r)$  auf, die im Quellpunkte  $Q$  regulär sind, die jedoch nicht mit Hilfe der Operatoren (1.4) aus einem Elementargesetz  $\varphi = \varphi(r)$  herstellbar sind. Als Beispiel diene die Potentialgleichung  $\Delta u = 0$ , die Lösungen von der Gestalt

$$Y_{lm}(\vartheta, \varphi) \frac{1}{r^{l+1}} \quad (1.8a)$$

und

$$Y_{lm}(\vartheta, \varphi) r^l \quad (1.8b)$$

aufweist. Während die Felder (1.8a) mit Hilfe des Operators (1.4) aus dem Elemen-



targesetz  $\varphi(r) = 1/r$  erhältlich sind, muß man zur Gewinnung von (1.8b) ein anderes in A im § 5 angegebenes Verfahren benutzen.

Um eine Verallgemeinerung der Klasse der Felder zu erhalten, die durch Differentialgleichungen von Typus (1.6) dargestellt werden, wäre es daher folgerichtig den Begriff der zu Elementargesetzen gehörigen linearen Felder weiter zu fassen:

1. Man müßte auch solche lineare Felder in Betracht ziehen, die durch Summen von Feldern (1.1) mit verschiedenen Elementargesetzen  $\varphi = \varphi(r)$  festgelegt werden.

2. Man müßte neben den Funktionen  $Y_{lm}(\vartheta, \varphi) R_l^{l+2s}(r)$  auch die nicht mit Hilfe der Operatoren (1.4) herstellbaren Funktionen  $Y_{lm}(\vartheta, \varphi) S_l^{l+2s}(r)$  in Betracht ziehen.

Wir wollen jedoch hier die durch Berücksichtigung der beiden oben angeführten Umstände entstehenden Komplikationen vermeiden und definitionsgemäß das Feld  $F(x, y, z)$  (1.1) oder  $F(r, \vartheta, \varphi)$  (1.7) als das durch das Elementargesetz  $\varphi = \varphi(r)$  gegebene Feld ansehen. Eine Änderung des Endresultates unserer Überlegungen dürfte dadurch wohl nicht eintreten.

## § 2. Randwertaufgaben im Gebiete linearer Felder, die durch Elementargesetze definiert werden

In der vorliegenden Note wollen wir zeigen, daß in der Klasse der linearen Skalarfelder, die in einem isotropen und homogenen Raume durch Elementargesetze bestimmt sind, sich die Felder die einer partiellen Differentialgleichung (1.6) genügen, auch noch durch eine andere Eigenschaft auszeichnen. Um sie aufzufinden stellen wir uns die bereits in A formulierte, dort aber nicht beantwortete Frage: Welche Bedingungen muß ein lineares, in einem isotropen und homogenen Raume durch ein Elementargesetz  $\varphi = \varphi(r)$  definiertes Skalarfeld erfüllen, damit man für dieses Feld „vernünftige“ Randwertaufgaben stellen kann, d. h. solche, deren Lösungen durch eine endliche Anzahl von Randbedingungen eindeutig festgelegt werden. Als solche wollen wir etwa die Vorgabe der Werte von

$$F, \frac{\partial F}{\partial N}, \frac{\partial^2 F}{\partial N^2}, \dots, \frac{\partial^{p-1} F}{\partial N^{p-1}} \quad (2.1)$$

an den Begrenzungsflächen des Raumes wählen, in dem das Randwertproblem vorgegeben ist. Mit  $N$  bezeichnen wir dabei die äußere Normale an diese Flächen.

Wir nehmen an, daß der Raum, für den wir das Randwertproblem zunächst lösen wollen, durch den Außen- oder Innenraum einer Kugel gegeben wird, in deren Mittelpunkt sich der Quellpunkt  $Q$  befindet. Es könnte vielleicht scheinen, daß man aus einem so speziellen Beispiel keine weitreichenden Schlüsse ziehen könnte. In Wirklichkeit können wir jedoch schon von vornherein feststellen: Sollte es sich zeigen, daß Felder  $F(x, y, z)$  (1.1) oder  $F(r, \vartheta, \varphi)$  (1.7) existieren für die wir keine „vernünftigen“ Randwertprobleme für den Außen- oder Innenraum einer Kugel lösen können, so dürfen wir selbstverständlich nicht behaupten, daß solche Probleme für Bereiche von beliebiger Gestalt lösbar sind.

Die vorgegebenen Randwerte können wir auf der Kugeloberfläche nach Kugelfunktionen  $Y_{lm}(\vartheta, \varphi)$  entwickeln. Es sei etwa

$$\frac{\partial^\sigma F}{\partial N^\sigma} = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} d_{lm}^\sigma Y_{lm}(\vartheta, \varphi). \quad (2.2)$$

Entscheiden wir uns für den Innenraum einer Kugel so ist  $\partial/\partial N = \partial/\partial r$  und aus (1.7) und (2.2) folgt dann daß

$$d_{lm}^\sigma = \sum_{s=0}^{\infty} c_{lm}^s \frac{d^\sigma}{dr^\sigma} R_l^{l+2s}(r) \Big|_{r=r_0} \quad (2.3)$$

wo  $r_0$  den Radius der Kugel bedeutet. Mit Rücksicht auf (1.5) gilt nun:

$$\begin{aligned} \frac{d}{dr} R_l^{l+2s}(r) &= \frac{l}{r} R_l^{l+2s}(r) + R_{l+1}^{l+1+2s}(r), \\ \frac{d^2}{dr^2} R_l^{l+2s}(r) &= \frac{l(l-1)}{r^2} R_l^{l+2s}(r) + \frac{2l+1}{r} R_{l+1}^{l+1+2s}(r) + R_{l+2}^{l+2+2s}(r), \\ &\dots \dots \dots \end{aligned} \quad (2.4)$$

Aus (2.3) und (2.4) folgt jedoch das Bestehen der Beziehungen:

$$\begin{aligned} d_{lm}^0 &= \sum_{s=0}^{\infty} c_{lm}^s R_l^{l+2s}(r_0), \\ d_{lm}^1 - \frac{l}{r_0} d_{lm}^0 &= \sum_{s=0}^{\infty} c_{lm}^s R_{l+1}^{l+1+2s}(r_0), \\ d_{lm}^2 - \frac{2l+1}{r_0} d_{lm}^1 + \frac{l(l+2)}{r_0^2} d_{lm}^0 &= \sum_{s=0}^{\infty} c_{lm}^s R_{l+2}^{l+2+2s}(r_0), \\ &\dots \dots \dots \\ d_{lm}^{p-1} \pm \dots &= \sum_{s=0}^{\infty} c_{lm}^s R_{l+p-1}^{l+p-1+2s}(r_0). \end{aligned} \quad (2.5)$$

Falls nur  $p$  Randbedingungen vorgegeben sind, so müßten bei festen  $l$ - und  $m$ -Werten die  $p$  Konstanten  $d_{lm}^\sigma$  ( $\sigma = 0, 1, 2, \dots, p-1$ ) eine unendliche Anzahl von Konstanten  $c_{lm}^{l'}$  festlegen, vorausgesetzt daß die Funktionen  $R_{l'}^{l'+2s}(r_0)$  ( $l' = l, l+1, l+2, \dots$ ) mit einem bestimmten  $l'$ -Wert für alle  $s$ -Werte von einander linear unabhängig sind. Die Lösung des Randwertproblems würde also in diesem Falle nicht eindeutig bestimmt sein.

Insbesondere müssen die linearen Gleichungen (2.5) auch im Falle  $l = m = 0$  erfüllt sein. Gemäß (1.5) ist jedoch in diesem Falle

$$R_0^{2s}(r) = \Delta^s \varphi(r) \quad (2.6)$$

Damit also insbesondere in der ersten Gleichung (2.5) im Falle  $l = m = 0$  nur eine endliche Anzahl linear unabhängiger  $R_0^{2s}(r_0)$  (2.6) auftritt, muß zwischen ihnen eine lineare Beziehung bestehen, die wir stets in der Gestalt

$$\sum_{i=0}^n a_i \Delta^i \varphi(r) = 0 \quad (a_n \neq 0) \quad (2.7)$$

voraussetzen können.

Wir wollen uns zunächst überzeugen, daß beim Erfülltsein von (2.7) in der ersten Gleichung (2.5) im Falle  $l = m = 0$  nur  $n$  linear unabhängige

$$R_0^{2s}(r_0) = \Delta^s \varphi(r) |_{r=r_0} \quad (s = 0, 1, 2, \dots, n-1) \quad (2.8)$$

auftreten. Mit Rücksicht auf (2.8) geht ja die erste Gleichung in (2.5) in unserem Falle über in

$$d_{00}^0 = \sum_{s=0}^{\infty} c_{00}^s \Delta^s \varphi(r) |_{r=r_0}. \quad (2.9)$$

Mit Hilfe von (2.7) können wir hier  $\Delta^n \varphi(r) |_{r=r_0}$  durch die  $\Delta^i \varphi(r) |_{r=r_0}$  mit  $i = 0, 1, 2, \dots, n-1$  ausdrücken. Wendet man auf (2.7) den Laplaceschen Operator  $\Delta$  an, so kann man  $\Delta^{n+1} \varphi(r) |_{r=r_0}$  durch die  $\Delta^i \varphi(r) |_{r=r_0}$  mit  $i = 1, 2, 3, \dots, n$  darstellen u. s. w. Auf diese Weise erkennt man, daß beim Bestehen der Beziehung (2.7) in der Summe (2.9) für  $d_{00}^0$  nur die ersten  $n$  Ausdrücke  $\Delta^s \varphi(r) |_{r=r_0}$  ( $s = 0, 1, 2, \dots, n-1$ ) auftreten und daher diese Summe die Gestalt

$$d_{00}^0 = \sum_{s=0}^{n-1} C_{00}^s \Delta^s \varphi(r) |_{r=r_0} \quad (2.10)$$

annimmt. Die Koeffizienten  $C_{00}^s$  werden durch gewisse unendliche Summen gegeben, in denen die Koeffizienten  $c_{00}^s$  und  $a_i$  auftreten.

Besteht nun eine Beziehung von der Gestalt (2.7) zurecht, so reduzieren sich im Falle  $l = m = 0$  alle Summen in (2.5) in der Weise, daß sie zu endlichen Summen werden, die jedoch alle die gleichen, nämlich die in (2.10) auftretenden Koeffizienten  $C_{00}^s$  enthalten. Die lineare Beziehung (2.7) zwischen den  $\Delta^s \varphi(r) = R_0^{2s}(r)$  besteht nämlich unabhängig vom  $l$ -Wert auch zwischen den  $R_l^{l+2s}(r)$ . Man braucht ja bloß den Operator  $Y_{lm} \left( \frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right)$  auf die Differentialgleichung (2.7) anzuwenden, um mit Rücksicht auf (1.4) die Beziehung

$$\sum_{i=0}^n a_i R_l^{l+2i}(r) = 0 \quad (a_n \neq 0) \quad (2.11)$$

für beliebige  $l$  mit den in (2.7) auftretenden Koeffizienten  $a_i$  zu erhalten.

Aus der Relation (2.11) kann man aber auch folgern, daß für jedes beliebige  $l$ ,  $m$ -Wertepaar die Summen in (2.5) die Gestalt

$$\sum_{s=0}^{n-1} C_{lm}^s R_l^{l'+2s}(r_0) \quad (l' = l, l+1, l+2, \dots) \quad (2.12)$$

annehmen. Es treten somit bei gegebenem  $l, m$  in jeder Summe in (2.5) die gleichen Koeffizienten  $C_{lm}^s$  auf. Das lineare Gleichungssystem (2.5) geht daher in ein Gleichungssystem für die  $n$  Koeffizienten  $C_{lm}^s$  über. Ist somit die Anzahl  $p$  der Randbedingungen (2.1) gleich  $n$ , so ist das aus den  $n$  Gleichungen (2.5) bestehende lineare Gleichungssystem im allgemeinen auflösbar. Es können somit  $p = n$  Randbedingungen (2.1) befriedigt werden, so daß das gestellte Randwertproblem für den Innenraum der Kugel lösbar ist.

Eine Nichtauflösbarkeit des Gleichungssystems (2.5) ist nur für solche Werte  $r_0$  des Kugelradius zu erwarten, für die die (2.12) entsprechenden Determinante  $|R_l^{l+2s}(r_0)|$  verschwindet. Dies kann selbstverständlich nur für besondere Elementargesetze  $\varphi = \varphi(r)$  eintreten. Ein bekanntes Beispiel ist das Elementargesetz  $\varphi(r) = \sin kr/r$  der Wellengleichung  $\Delta u + k^2 u = 0$ , wo  $n = 1$  ist.

Mit Rücksicht darauf, daß das Feld  $F(x, y, z)$  in der Gestalt (1.1) darstellbar ist, folgt aber aus (2.7) ebenso wie in A, daß es eine Lösung der Differentialgleichung (1.6) ist. Unter dieser Voraussetzung ist das Randwertproblem (2.1) selbstverständlich nicht nur für die Kugel, sondern auch für einen Raum von beliebiger Gestalt lösbar.

Die Tatsache, daß wir hier ebenso wie in A auf die Differentialgleichung (2.7) für das Elementargesetz  $\varphi = \varphi(r)$  stoßen, bedeutet daß die in A gestellte Forderung mit der hier formulierten äquivalent ist. Sowohl die Forderung, daß die Anzahl der linear unabhängigen Kugelfunktionenmultipole mit einer bestimmten Kugelfunktion  $Y_{lm}(\vartheta, \varphi)$  eine endliche ist, als auch die Forderung der Lösbarkeit der Randwertaufgabe (2.1) führen zu dem Ergebnis, daß das Feld  $F(x, y, z)$  (1.1) oder das ihm äquivalente Feld (1.7) der partiellen Differentialgleichung (1.6) genügen muß.

Interessant ist die Frage, warum wir hier sowie in A auf eine partielle Differentialgleichung stoßen, die gerade die Gestalt (1.6) hat. Diese Frage beantwortet sich dahin, daß dies bekanntlich die einzige lineare Differentialgleichung für ein Skalarfeld im dreidimensionalen Raume ist, die invariant ist gegenüber der Gruppe der Verschiebungen und der Rotationen. Statt  $F(x, y, z)$  können in (1.6) bei den einzelnen Gliedern Summen von beliebigen zeitlichen Ableitungen der Funktion  $F(x, y, z)$  auftreten.

Bezüglich der Feldtheorie der Elementarteilchen sei hier nachstehendes bemerkt: Die in der vorliegenden Note dargestellten Überlegungen sind im allgemeinen auf sie nicht anwendbar. Es hat ja doch in dieser Theorie keinen Sinn Randwertaufgaben zu stellen. Von diesem Gesichtspunkte aus wären somit hier Felder die nur durch Elementargesetze definiert werden können, zulässig. Man könnte dann jedoch eine solche Theorie nicht auf einer Langrangeschen Funktion aufbauen, da ja aus dem Lagrangeschen Formalismus zwangsläufig als Feldgleichungen sich partielle Differentialgleichungen ergeben.

Es ist ferner auch nicht abzusehen, wie man ein, nur auf einem Elementargesetz aufgebautes Feld quantisieren könnte. Daß skalare Felder von der Gestalt (1.2)



gemeinsame Eigenlösungen der Operatoren des Quadrates des gesamten Impulsmomentes und seiner  $z$ -Komponente sind, bedeutet ja doch noch nicht eine vollständige Quantisierung des Feldes. Es fehlt hier doch noch die Quantisierung der Radialfunktion.

Krynica, im August 1959.

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RELATIVISTIC HYDRODYNAMICS OF ROTATING FLUID  
MASSES MOVING WITH THE VELOCITY OF LIGHT

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Wir verallgemeinern eine ursprünglich von Weyssenhoff vorgeschlagene Methode und beobachten das Verhalten von relativistischen flüssigen Tropfen bei Geschwindigkeiten, die derjenigen des Lichtes gleich sind (oder nahe kommen). Es folgt daraus, dass für  $v = c$  neue qualitative Eigentümlichkeiten auftauchen und dass Tensor-Größen durch Pseudotensoren, im Sinne Weyssenhoffs ersetzt werden. Als Beispiel geben wir die vollkommene, aus Tröpfchen bestehende Flüssigkeit mit einer nicht nennenswerten Restmasse und zeigen dass, wenn wir sie mit einer einfachen Verbindung zusammenbringen, die daraus entstehende Flüssigkeit genau der vor kurzem von Lee und Yang vorgeschlagenen, zweikomponenten Neutrinotheorie entspricht.

*Introduction*

In two recent papers the general theory of relativistic fluid masses was treated from two different points of view. In the first, Bohm<sup>1</sup> and one of us (J.-P. V.) have established directly the physical signification of the well-known Weyssenhoff equations of motion for such bodies. With the help of the new concept of center of matter density (which corresponds to the classical notion of geometrical body center in non relativistic mechanics) it can be shown that these equations represent the relative behaviour of this new center with respect to the usual center of mass. In the second paper<sup>2</sup> we gave (in collaboration with F. Halbwachs) a Lagrangian formulation of these equations with the help of a set of kinematical variables describing the rotational orientation of the element of the fluid which we call Einstein-Kramers variables. The utilization of these variables is valuable for various reasons which we have exposed elsewhere.<sup>3</sup>

<sup>1</sup> D. Bohm and J.-P. Vigier, *Phys. Rev.*, **109**, 1882, (1958).

<sup>2</sup> P. Hillion, F. Halbwachs and J.-P. Vigier, Lagrangian formalism in relativistic hydrodynamics of rotating fluid masses published in *Nuovo Cimento*, **10**, 817 (1958).

<sup>3</sup> See ref. 2 and also F. Halbwachs, Thesis (Paris) to be Published at Gautier-Villars, (1959) under the title „Recherches sur la dynamique du corpuscule tournant relativiste et l'hydrodynamique des fluides à spin“.

In this paper, however, we want to study a special case of the latter formalism, namely the physical behaviour of rotating fluid masses for velocities approaching the velocity of light.

This problem is interesting for three main reasons. In the first place, the study of the classical behaviour of extended bodies at such velocities might give useful indications on the behaviour of matter in the high energy domain: in particular for temperatures corresponding to such velocities. This should eventually be applied to the theory of collective excitation in high energy plasmas, and to the so-called cosmic "jets".

Secondly, it might pave the way for a quantization of classical extended bodies when  $v = c$ .

Lastly, as we shall see, a perfect continuous fluid of a special type of relativistic fluid droplets with vanishing rest mass connected by simple tensions satisfies exactly the laws of motion of a two component neutrino field.

We wish to stress, however, that independently of these applications the question of the behaviour of particles extended in space for velocities approaching the velocity of light is interesting as such. So far as we know it has never been treated except in a qualitative way.<sup>4</sup> This is only natural as long as one remains attached to the basis idea that particles are point-like and devoid of internal structure.

Evidently in that case all that is needed classically is the description of the particle world-lines. On the contrary if the particles can be described by an energy momentum density  $T_{\mu\nu}$ , and current density  $j_\mu$  enclosed within a time-like tube it is clear that they will be modified by external motion. For example, the particles shape flattens perpendicularly to the velocity as a consequence of the Lorentz contraction and, at the limit  $v = c$ , is reduced to a plane section. For high acceleration its various points contract at different rates thus modifying the internal distribution of matter and energy.

In this paper, we shall show that the kinematical variables introduced by Einstein and Kramers (which we have used to describe the internal states of the relativistic fluid masses) provide a convenient way to treat this problem mathematically. In section 1 we shall give a brief summary of the Lagrangian formalism in terms of the E. K. variables. In section 2 we shall see what happens to these variables when the velocity is increased up to the velocity of light. In section 3 finally, according to the preceding discussion, we shall study a particular case of relativistic fluid droplets which when accelerated up to the velocity of light and coupled in a simple way, behave like neutrinos satisfying the two component spinor theory recently proposed by Lee and Yang.<sup>5</sup>

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<sup>4</sup> With the exception of an attempt by Weyssenhoff, *Acta phys. Polon.*, **9**, 7 (1947).

<sup>5</sup> T. D. Lee and C. N. Yang, *Phys. Rev.*, **105**, 1671, (1957).

A. Salam, *Nuovo Cimento*, **5**, 299 (1957).

L. Landau, *Nuclear Physics*, **3**, 127 (1957).



## § 1.

As is well known the study of extended relativistic fluid droplets rests on the idea that one can introduce integral quantities which correspond to average or global properties of the body. In this way the study of the internal complex motions can be left aside and replaced in the first approximation, by the laws of motion which govern these global quantities.

We thus start<sup>6</sup> from the basic assumption that the particle is comparable to a fluid mass with conserved energy momentum density  $T_{\mu\nu}$  and current density  $j_\mu$  which vanish outside of a time-like tube defining the physical limit of the droplet. One then defines immediately six physically important global quantities, namely:

— The total energy momentum vector

$$G_\mu = \frac{1}{ic} \int_{\Sigma} T_{\mu 4} dv$$

(where  $dv$  denotes a three dimensional volume element of a plane section  $\Sigma$ ) which determines the inertial Lorentz frame  $\Pi_0$  (in which  $G_i = 0$ ).

— The centers  $X$  and  $Y$  of mass and matter density defined in  $\Pi_0$  by the relations

$$X_k^0 \left\{ \int_{\Sigma_0} T_{44}^0 dv_0 \right\} = \int_{\Sigma_0} x_k^0 T_{44}^0 dv^0;$$

and

$$Y_k^0 \left\{ \int_{\Sigma_0} j_4^0 dv^0 \right\} = \int_{\Sigma_0} x_k^0 j_4^0 dv^0;$$

the latter moving along a world-line with the unitary tangent four velocity  $v_\mu$ . The index 0 denotes the fact that the quantities are evaluated in the frame  $\Pi_0$ .

— The angular momentum  $M_{\mu\nu}$  with respect to the center of matter density

$$M_{\mu\nu} = \frac{1}{ic} \int_{\Sigma_0} [(x_\mu - Y_\mu) T_{\nu 4} - (x_\nu - Y_\nu) T_{\mu 4}] dv$$

Now, if we denote by  $\dot{A}$  the derivation of a quantity  $A$  along the world-line followed by the center of matter density ( $\dot{A} = v_\lambda \partial_\lambda A$ ) we can establish the fundamental laws of motion

$$\begin{aligned} \dot{G}_\mu &= 0 \\ \dot{M}_{\mu\nu} &= G_\mu v_\nu - G_\nu v_\mu \end{aligned} \quad (1)$$

<sup>6</sup> See references (1). From now on we shall use the same notations. Greek indices  $\mu$  vary from one to four and denote the usual tensor indices — latin indices vary from one to three and denote space — like components — indices repeated twice are summed over all possible values — We work in Minkowski's space time.

which combined with a Weyssenhoff-like condition (such as  $M_{\mu\nu} v_\nu = 0$ ) determine completely the behaviour of the global quantities attached to the droplet. If instead of a single droplet one considers a perfect macroscopic fluid<sup>7</sup> made of such droplets one can define, instead of the preceding tensors, density relations obtained by multiplying (1) by the scalar density  $\varrho$  and adding to them the relation

$$\dot{\varrho} = \partial_\mu (\varrho v_\mu) = 0$$

As was pointed out elsewhere, this procedure has the advantage of introducing into the formalism the mathematical methods of field theory and involves no disadvantage since the droplets are assumed not to interact.

The passage to Lagrangian formalism rests on the introduction of the Einstein-Kramers variables. They consist of an orthogonal set of four unitary vectors  $a_\mu^{(\xi)}$  (The index  $\xi$  varies also from one to four though it does not mean a vector index) one of which  $a_\mu^{(4)}$  is identical to  $v_\mu$ . This frame is attached to the center of matter density of each droplet which constitutes the macroscopic fluid, and its rotation represents the instantaneous rotation of the droplet through the relations

$$\omega_{\mu\nu} = \frac{1}{2} (\dot{a}_\mu^{(\xi)} a_\nu^{(\xi)} - a_\mu^{(\xi)} \dot{a}_\nu^{(\xi)})$$

which determine the angular four velocity.

We are now in a position to demonstrate the following general theorem<sup>8</sup>. If in the first approximation  $M_{\mu\nu}$  is a general function of the  $a_\mu^{(\xi)}$  and not of their derivatives, the equations of motion (1) are just the conservation equations associated with the Lagrangian

$$L = \frac{1}{2} \varrho M_{\alpha\beta} \omega_{\alpha\beta} + \varrho m_0 c^2 + ic\varrho a_\mu^4 \partial_\mu S + \lambda_{\mu\nu} (a_\mu^{(\xi)} a_\nu^{(\xi)} - \delta_{\mu\nu})$$

The physical signification of each term is clear. the first term  $\frac{1}{2} \varrho M_{\alpha\beta} \omega_{\alpha\beta}$  corresponds to the rotation energy, the second  $m_0 c^2$  to the rest mass energy, the third to the conservation of current and the last to the orthogonolity and unitary conditions of the  $a_\mu^{(\xi)}$  variables.

The demonstration of this theorem is simple. It has been established by Belinfante and Rosenfeld that the canonical energy momentum tensor deduced from a Lagrangian  $L$  of variables  $q_\lambda$  namely:  $t_{\mu\nu} = \frac{\partial L}{\partial(\partial_\nu q_\lambda)} \partial_\mu q_\nu - \delta_{\mu\nu} L$

is conserved as a consequence of the field equations, namely

$$\partial_\nu t_{\mu\nu} = 0 \quad (2)$$

If we can write  $\varrho M_{\alpha\beta}$  as  $m_{\alpha\beta}$  where  $m_{\alpha\beta} (a_\mu^{(\xi)})$  is the average angular momentum of the droplets which constitute the macroscopic fluid at a given point (so that the

<sup>7</sup> In hydrodynamics this means a fluid without sources or sinks made of such elements without interaction; the center of matter density of each droplet following a given line of flow.

<sup>8</sup> Which generalizes the results of reference (2).

total Lagrangian is just the Lagrangian of the individual droplets  $\frac{1}{2} M_{\alpha\beta} \omega_{\alpha\beta} + m_0 c^2 + \partial_{\mu\nu} (a_\mu^{(\xi)} a_\nu^{(\xi)} - \delta_{\mu\nu})$  multiplied by  $\varrho$  plus the Lagrange conservation condition  $ic\varrho a_\mu^{(4)} \partial_\mu S$  we get by variation with respect to  $\varrho$  and using  $a_\mu^{(\xi)} a_\nu^{(\xi)} = \delta_{\mu\nu}$ :

$$L = 0.$$

As a consequence the energy momentum tensor  $t_{\mu\nu}$  becomes:

$$t_{\mu\nu} = g_\mu v_\nu$$

with  $g_\mu = \varrho (\partial_\mu S + \frac{1}{2} m_{\mu\nu} a_\alpha^{(\xi)} \partial_\mu a_\beta^{(\xi)}) = \varrho G_\mu$  and the corresponding conservation relation  $\partial_\nu t_{\mu\nu} = 0$  can be written:

$$\dot{g}_\mu = 0 \quad (3)$$

In the case of density quantities, the dot implies, as it is well-known, the derivative along the local current line, that is:  $\dot{g}_\mu = \partial_\nu (v_\nu g_\mu)$

The next step is to write the second Rosenfeld-Belinfante conservation relation:

$$\partial_\lambda f_{\mu\nu\lambda} = \frac{1}{2} (t_{\mu\nu} - t_{\nu\mu}) \quad (4)$$

where

$$f_{[\mu\nu]\lambda} = \mathfrak{T}_{[\mu\nu]}^{rs} \frac{\partial L}{\partial (\partial_\lambda q_r)} q_s$$

$\mathfrak{T}$  representing the infinitesimal Lorentz transform on the variables  $a_\mu^{(\xi)}$  that is

$$\mathfrak{T}_{\mu\nu}^{\alpha\beta} = \frac{1}{2} (\delta_{\alpha\mu} \delta_{\beta\nu} - \delta_{\alpha\nu} \delta_{\beta\mu})$$

This gives immediately as a consequence of our assumptions

$$f_{\mu\nu\lambda} = \frac{ic}{2} m_{\mu\nu} a_\lambda^{(4)}$$

and relation (4) becomes

$$\varrho \dot{M}_{\mu\nu} \equiv \dot{m}_{\nu\mu} = g_\mu v_\nu - g_\nu v_\mu \quad (5)$$

(with  $v_\nu = ic a_\nu^{(4)}$ ,  $h_0^2 = |M_{\alpha\beta}|$  and  $\varrho M_{\alpha\beta} = m_{\alpha\beta}$ ). This demonstrates our theorem since relations (2) and (3) are evidently identical with equations (1).

We notice further that any given form of  $m_{\alpha\beta}$  will then correspond to a particular type of internal motion. For example one could start from a Lagrangian satisfying Weyssenhoff's condition

$$L = \varrho m_0 c^2 + ic\varrho a_\mu^{(4)} \partial_\mu S + ic\varrho h_0 a_\mu^{(4)} a_\lambda^{(1)} \partial_\mu a_\lambda^{(2)} + \varrho \lambda_{\mu\nu} (a_\mu^{(\xi)} a_\nu^{(\xi)} - \delta_{\mu\nu}) \quad (6)$$

which we shall utilize later. In this Lagrangian:

$$a_\mu^{(4)} = v_\mu / ic; \quad a_\mu^{(3)} = \frac{i}{2c\varphi h_0} \varepsilon_{\mu\nu\alpha\beta} v_\nu m_{\alpha\beta} \quad (7)$$

$$a_\mu^{(1)} = \varepsilon_{\mu\nu\alpha\beta} a_\alpha^{(3)} a_\beta^{(4)} a_\nu^{(2)}; \quad a_\mu^{(2)} = -\varepsilon_{\mu\nu\alpha\beta} a_\alpha^{(3)} a_\beta^{(4)} a_\nu^{(1)}$$

## § 2

According to our program the next step is to see what happens to this formalism for velocities approaching the velocity of light. This could be attempted in various ways. The first and most straight forward is just to accelerate the particle in a given direction and apply the usual corresponding Lorentz formulas to all tensor quantities. We have attempted that but it leads to very complex calculations which finally give the same results as the more simple and powerful method which we shall now develop; so we shall not discuss it in this paper.

This other method rests on a very simple remark made by Weyssenhoff. If one follows the world-line of any given particle (in our case the motion of the center of matter density), the most natural parameter is the proptime  $\tau$  on that line ( $-c^2 d\tau^2 = dx_\alpha dx_\alpha$ ). Now, if that line becomes tangent to the light cone  $d\tau = 0$  and  $\tau$  loses all physical significance. This shows that relations (1) which depend on  $\tau$  must be transformed for  $v = c$  and that  $\tau$  is not a suitable parameter for such velocities. Accordingly Weyssenhoff proposed to drop  $\tau$  as parameter and to replace it by another parameter  $p$  on the world-line, such that  $p$  will still flow even when it becomes tangent to the light cone. The only restriction on  $p$  is to impose upon it the restriction

$$\tau' \equiv \frac{d\tau}{dp} \geq 0$$

so that the condition  $\tau' \rightarrow 0$  implies  $d\tau = 0$  which means the particle moves with the velocity  $c$ . One can then define the world-line followed by the center of matter density not by the unit vector:

$$ic a_\alpha^{(4)} = \frac{dx_\alpha}{d\tau},$$

but by another vector:

$$w_\alpha = \frac{dx_\alpha}{dp}$$

so that:

$$w_\alpha = ic \tau' a_\alpha^{(4)}$$

and

$$w_\alpha w_\alpha = -c^2 \tau'^2$$

If  $\tau' \rightarrow 0$  we then get

$$w_\alpha w_\alpha = 0$$

and the world-line becomes tangent to the light cone. In order to avoid confusion it is necessary to stress the fact that  $w_\alpha$  is not an ordinary four vector but a four vector



depending on the parametrization; its four components transform like components of a four vector when the coordinates are transformed without change of parametrization, but they are all multiplied by a common factor  $dp/d\bar{p}$  when the parametrization is changed from  $p$  to  $\bar{p}$ .

As Weyssenhoff remarked it is even possible in a given frame to take as parameter the ordinary time  $t = x_4/c$ . In this case we change the parametrization for every change of coordinate system in such a way that  $p$  remains equal to  $t$  in the coordinate system of interest. Then  $w_\alpha$  becomes  $u_\alpha = x_\alpha/dt$  with the components<sup>9</sup>  $(\vec{u}, ic)$ . It is then evident that the four quantities  $u_\alpha$  do not form a four vector neither in the ordinary sense, nor a four vector depending on the parametrization (this would only be the case if  $p$  was a scalar parameter) but form instead a new geometrical object which we can call "pseudo-vector". The components of such a pseudo-vector transform like the components of vector but with an additional multiplication factor  $dt/d\bar{t} = dx^4/dx_4$  when we pass from the frame  $\Sigma$  to a frame  $\bar{\Sigma}$ . The magnitudes of a pseudo-vector  $(u_\alpha u_\alpha)^{1/2}$ , or any scalar product such as  $(G_\alpha u_\alpha)^{1/2}$  behave like "pseudo-scalars" and are also multiplied by  $dt/d\bar{t}$  in the case of a Lorentz transformation. As a consequence, the pseudo-vector  $u_\alpha$  has, in all possible frames, the ordinary velocity  $\vec{v}$  as space components and  $c$  as time-component. In the limit  $v = c$  one gets evidently:

$$u_\alpha u_\alpha = 0.$$

Weyssenhoff's method for the passage to velocities approaching the velocity of light is now clear. In any equation one replaces derivatives with respect to the proper time  $\tau$  by the expression:

$$\frac{d}{d\tau} = \frac{dt}{d\tau} \cdot \frac{d}{dt}$$

and pass to the limit by pushing  $\tau'$  to zero. More generally one can write laws of motion in terms of any parameter  $p$ , satisfying the condition  $\tau' \equiv d\tau/dp \geq 0$  and pass to the limit  $\tau' = 0$ .

To illustrate this general method, let us treat briefly the problem of the limit of Weyssenhoff's equations for a particle moving with the velocity of light.

Let us choose as parameter the ordinary time  $t$   $\left( \tau' = \frac{d\tau}{dt} \right)$  and denote by  $f'$  the time derivative of a given quantity  $f$  so that:

$$f' = \frac{df}{d\tau} = \partial_4 f + u_k \partial_k f \quad (k = 1, 2, 3)$$

If we now take for example the relation

$$\dot{G}_\mu = 0$$

<sup>9</sup> The  $\vec{u}$  designs a three vector.

it can be written  $\frac{dt}{d\tau} \frac{d}{dt} G_\mu = \frac{1}{\tau'} \frac{d}{dt} G_\mu = 0$

When  $\tau' \rightarrow 0$  this implies

$$G'_\mu = 0.$$

Applying the same reasoning to the other equations (1) one obtains the following laws of motion:

$$G'_\alpha = 0$$

$$M'_{\alpha\beta} = G_\alpha u_\beta - G_\beta u_\alpha$$

$$M_{\alpha\beta} u_\beta = 0$$

If we start instead from  $G_\mu = m_0 v_\mu + \frac{1}{c^2} M_{\mu\nu} \dot{v}$  and multiply both members by  $\tau'^2$  we get:

$$G_\mu \tau'^2 = m_0 u_\mu \tau' + \frac{1}{c^2} M_{\mu\nu} u'_\nu.$$

The left hand side goes to zero with  $\tau'$  and multiplying by the matter density  $\varrho$  we find for  $v \rightarrow c$

$$\mu'_0 u_\mu + \frac{1}{c^2} m_{\mu\nu} u'_\nu = 0$$

with

$$\mu'_0 = \frac{1}{c^2} g_\mu u_\mu = \varrho m_0 \tau'.$$

This implies that we introduce a density  $\mu'_0$  of proper mass which goes to zero with  $\tau'$  since it would take an infinite energy to push a non zero rest mass particle to the velocity of light.

As a consequence the equations of motion for a fluid of Weyssenhoff particles can be written:

$$\varrho' = 0 \quad g'_\mu = 0 \quad m'_{\mu\nu} = g_\mu u_\nu - g_\nu u_\mu$$

$$m_{\mu\nu} u_\nu = 0, \quad g_\mu u_\mu = 0 \quad m_{\mu\nu} u'_\nu = 0.$$

Of course, these relations are not independent and reduce to the set:

$$G'_\mu = 0 \quad (8a) \quad M'_{\mu\nu} = G_\mu u_\nu - G_\nu u_\mu \quad (8d)$$

$$G_\mu u_\mu = 0 \quad (8b) \quad M_{\mu\nu} u_\mu = 0 \quad (8e)$$

$$\varrho' = 0 \quad (8c) \quad (8)$$

However, this procedure of Weyssenhoff is rather cumbersome since it implies going to the limit of every equation of motion separately and in more complex cases, generalizing his simple model<sup>10</sup>, it proves often very difficult.

In order to avoid any trouble we therefore propose to generalize Weyssenhoff's idea in the following way:

If we utilize a Lagrangian formalism in terms of the E. K. variables the behaviour of particles for  $v \neq c$  is clearly determined by the corresponding Euler equations. As a consequence if we can determine the limit of these variables we can determine the corresponding limit of  $L$  for  $v \rightarrow c$  and deduce therefrom the corresponding laws of motion, which are just the limit of Euler's equations.

This reduces our problem to two steps:

- a. Determine the limit of the E. K. variables for  $v \rightarrow c$ ;
- b. Write the corresponding Lagrangian.

The determination of the limit of the E. K. variables can be worked out with the help of Weyssenhoff's pseudo-vectors when  $p = t$ . If we recall the definitions (7) we can write instead of  $a_\mu^{(4)}$  the vector  $\alpha_\mu^{(4)} = u_\mu/ic$  that is

$$\alpha_\mu^{(4)} = \tau' a_\mu^{(4)}$$

so that  $\alpha_\mu^{(4)} \alpha_\mu^{(4)} = 0$  for an isotropic world-line ( $\tau = 0$ ).

This relation can be written:

$$\alpha_\mu^{(4)} \alpha_\mu^{(4)} = \alpha_k^{(4)} \alpha_k^{(4)} + \alpha_4^{(4)} \alpha_4^{(4)} = 0 \quad (k = 1, 2, 3) \quad (9)$$

Let us now put  $p = t$  and work out the limit in that case.

We have  $u_\mu = \{\vec{u}, ic\}$   $\alpha_4^{(4)} = 1$  and we can replace  $\alpha_\mu^{(4)}$  by  $b_\mu^{(4)} = \{b_k^{(4)}, 1\}$  with the relation  $b_i^{(4)} b_i^{(4)} = -1$

In the same way, instead of  $a_\mu^{(3)} = \frac{i}{2c \rho h_0} t_{\mu\nu\alpha\beta} v_\nu m_{\alpha\beta}$

we can write:

$$\alpha_\mu^{(3)} = \frac{i}{2\rho ch_0} t_{\mu\nu\alpha\beta} u_\nu m_{\alpha\beta}$$

that is:

$$\alpha_\mu^{(3)} = \tau' a_\mu^{(3)} \quad \text{with} \quad \alpha_\mu^{(3)} \alpha_\mu^{(3)} = 0. \quad (10)$$

As we have:

$$a_\mu^{(3)} a_\mu^{(4)} = 0$$

we can also write:

$$\alpha_\mu^{(3)} \alpha_\mu^{(4)} = 0. \quad (11)$$

<sup>10</sup> Considered for example in ref. 2 and 3.

The three relations (9) (10) (11) evidently imply that

$$\alpha_{\mu}^{(3)} = \lambda \alpha_{\mu}^{(4)} \quad (12)$$

where  $\lambda$  is a constant.

This results immediately from the fact that

$$i \alpha_4^{(4)} = \sqrt{\sum_i (\alpha_i^{(4)})^2}, \quad i \alpha_4^{(3)} = \sqrt{\sum_j (\alpha_j^{(3)})^2}$$

and

$$- \alpha_{\mu}^{(4)} \alpha_{\mu}^{(3)} = \sqrt{\sum_i (\alpha_i^{(4)})^2} \sqrt{\sum_j (\alpha_j^{(3)})^2} - \alpha_k^{(4)} \alpha_k^{(3)} > 0$$

which results immediately from Schwartz' inequality. As one knows the equality sign is only possible when relation (12) is satisfied.

As we shall see later this relation implies that the spin is either parallel or antiparallel to the velocity, when  $v \rightarrow c$ .

Let us now consider the limit of  $\alpha_{\mu}^{(1)}$  and  $\alpha_{\mu}^{(2)}$ . These limits, which we shall call  $b_{\mu}^{(1)}$  and  $b_{\mu}^{(2)}$  satisfy evidently the relations

$$b_{\mu}^{(1)} b_{\mu}^{(4)} = 0 \quad b_{\mu}^{(1)} b_{\mu}^{(1)} = 1 \quad (13)$$

$$b_{\mu}^{(1)} b_{\mu}^{(4)} = 0 \quad b_{\mu}^{(2)} b_{\mu}^{(2)} = 1 \quad (14)$$

$$b_{\mu}^{(1)} b_{\mu}^{(2)} = 0 \quad b_{\mu}^{(4)} b_{\mu}^{(4)} = 0. \quad (15)$$

Let us denote by  $\beta_k^r$  ( $r = 1, 2, 4$ ) ( $k = 1, 2, 3$ ) the space components of the quantities  $\alpha_{\mu}^{(r)}$ . The relations (13), (14), (15) become for  $v \rightarrow c$

$$\begin{aligned} \beta_k^{(1)} \beta_k^{(4)} &= b_4^{(1)} b_4^{(4)} = b_4^{(1)} \\ \beta_k^{(2)} \beta_k^{(4)} &= b_4^{(2)} b_4^{(4)} = b_4^{(2)} \\ \beta_k^{(1)} \beta_k^{(2)} &= b_4^{(1)} b_4^{(2)} \\ \beta_k^{(1)} \beta_k^{(1)} &= 1 - (b_4^{(1)})^2 \\ \beta_k^{(2)} \beta_k^{(2)} &= 1 - (b_4^{(2)})^2 \end{aligned} \quad (16)$$

where the first member is the three dimensional scalar product. These five relations are equivalent to four independent relations. We still need four relations to determine  $b_{\mu}^{(1)}$  and  $b_{\mu}^{(1)}$  completely. To get them let us pass to the limit for  $v \rightarrow c$  of the definition of  $\alpha_{\mu}^{(3)}$ . We have:

$$\alpha_{\mu}^{(3)} = \varepsilon_{\mu\nu\alpha\beta} \alpha_{\nu}^{(4)} \alpha_{\alpha}^{(1)} \alpha_{\beta}^{(2)}.$$

The time component of  $\alpha_{\mu}^{(3)}$  becomes:

$$a_4^{(3)} = \varepsilon_{4ijk} a_i^{(4)} a_j^{(1)} a_k^{(2)}.$$

Multiplying both members by  $\tau'$  and taking the limit we get:

$$\begin{aligned} b_4^{(3)} &= \varepsilon_{4ijk} b_i^{(4)} b_j^{(1)} b_k^{(2)} \\ \beta_4^{(3)} &= \vec{\beta}^{(4)} \cdot (\vec{\beta}^{(1)} \wedge \vec{\beta}^{(2)}) \end{aligned}$$



where the symbol  $\wedge$  denotes the usual three dimensional vector product<sup>11</sup>. As  $b_4^{(3)} = \lambda b_4^{(4)}$  with  $\lambda = \text{constant}$ .

Then:

$$\lambda = \vec{\beta}^{(4)} (\vec{\beta}^{(1)} \wedge \vec{\beta}^{(2)}) \quad (17)$$

The space components of  $\alpha^{(3)}$  become

$$\begin{aligned} \beta_i^{(3)} &= b_i^{(3)} = \varepsilon_{ij4k} b_4^{(4)} b_j^{(1)} b_k^{(2)} + \varepsilon_{ij4k} b_j^{(4)} b_4^{(1)} b_k^{(2)} + \varepsilon_{ijk4} b_j^{(4)} b_k^{(1)} b_4^{(2)} \\ &= b_4^{(4)} (\vec{\beta}^{(1)} \wedge \vec{\beta}^{(2)}) + b_4^{(2)} (\vec{\beta}^{(4)} \wedge \vec{\beta}^{(1)}) + b_4^{(1)} (\vec{\beta}^{(2)} \wedge \vec{\beta}^{(4)}). \end{aligned}$$

Multiplying these relations by  $\tau'$  and going to the limit we get the vector relation (where  $b_4^{(r)}$  are numbers):

$$\vec{\beta}^{(3)} = b_4^{(4)} (\vec{\beta}^{(1)} \wedge \vec{\beta}^{(2)}) + b_4^{(2)} (\vec{\beta}^{(4)} \wedge \vec{\beta}^{(1)}) + b_4^{(1)} (\vec{\beta}^{(2)} \wedge \vec{\beta}^{(4)})$$

replacing  $\vec{\beta}^{(3)}$  by  $\lambda \vec{\beta}^{(4)}$  and noting  $\beta_4^{(4)} = 1$ , we find:

$$\lambda \vec{\beta}^{(4)} = \vec{\beta}^{(1)} \wedge \vec{\beta}^{(2)} + \vec{\beta}^{(4)} \wedge (b_4^{(2)} \vec{\beta}^{(1)} - b_4^{(1)} \vec{\beta}^{(2)}).$$

If we calculate now the product  $\lambda (\vec{\beta}^{(1)} \wedge \vec{\beta}^{(4)})$  we find

$$\lambda (\vec{\beta}^{(1)} \wedge \vec{\beta}^{(4)}) = \vec{\beta}^{(1)} \wedge \vec{\beta}^{(1)} \wedge \vec{\beta}^{(2)} + \vec{\beta}^{(1)} \wedge [\vec{\beta}^{(4)} \wedge (b_4^{(2)} \vec{\beta}^{(1)} - b_4^{(1)} \vec{\beta}^{(2)})]$$

taking into account the well-known vector relation

$$\vec{A} \wedge \vec{B} \wedge \vec{C} = (\vec{A} \cdot \vec{C}) \vec{B} - (\vec{A} \cdot \vec{B}) \vec{C}$$

the preceding relation becomes

$$\begin{aligned} \lambda (\vec{\beta}^{(1)} \wedge \vec{\beta}^{(4)}) &= (\vec{\beta}^{(1)} \cdot \vec{\beta}^{(2)}) \vec{\beta}^{(1)} - (\vec{\beta}^{(1)} \cdot \vec{\beta}^{(1)}) \vec{\beta}^{(2)} + \\ &+ [b_4^{(2)} (\vec{\beta}^{(1)} \cdot \vec{\beta}^{(1)}) - b_4^{(1)} (\vec{\beta}^{(2)} \cdot \vec{\beta}^{(1)})] \vec{\beta}^{(4)} - \\ &- (\vec{\beta}^{(1)} \cdot \vec{\beta}^{(4)}) (b_4^{(2)} \vec{\beta}^{(1)} - b_4^{(1)} \vec{\beta}^{(2)}). \end{aligned}$$

Taking into account relations (16) this equation can be written

$$\begin{aligned} \lambda (\vec{\beta}^{(1)} \wedge \vec{\beta}^{(4)}) &= b_4^{(1)} b_4^{(2)} \vec{\beta}^{(1)} - \vec{\beta}^{(2)} - (b_4^{(1)})^2 \vec{\beta}^{(2)} + [b_4^{(2)} + (b_4^{(1)})^2 b_4^{(2)} - \\ &- (b_4^{(1)})^2 b_4^{(2)}] \vec{\beta}^{(4)} - b_4^{(1)} (b_4^{(2)} \vec{\beta}^{(1)} - b_4^{(1)} \vec{\beta}^{(2)}) \quad \lambda (\vec{\beta}^{(1)} \wedge \vec{\beta}^{(4)}) = -\vec{\beta}^{(2)} + b_4^{(2)} \vec{\beta}^{(4)} \end{aligned}$$

so that

$$b_4^{(2)} \vec{\beta}^{(4)} = \vec{\beta}^{(2)} - \lambda (\vec{\beta}^{(4)} \wedge \vec{\beta}^{(1)}) \quad (18)$$

If we eliminate  $\beta^{(4)}$  between (17) and (15) we get

$$b_4^{(2)} \lambda = [\vec{\beta}^{(2)} - \lambda (\vec{\beta}^{(4)} \wedge \vec{\beta}^{(1)})] (\vec{\beta}^{(1)} \wedge \vec{\beta}^{(2)})$$

as

$$\vec{\beta}^{(2)} \cdot (\vec{\beta}^{(1)} \wedge \vec{\beta}^{(1)}) = 0$$

<sup>11</sup> The dot denotes the three dimensional scalar product.

then

$$b_4^{(2)} = -(\vec{\beta}^{(4)} \wedge \vec{\beta}^{(1)}) \cdot (\vec{\beta}^{(1)} \wedge \vec{\beta}^{(2)}).$$

Utilizing:

$$\vec{A} \cdot (\vec{B} \wedge \vec{C}) = \vec{C} \cdot (\vec{A} \wedge \vec{B})$$

we get

$$b_4^{(2)} = -\vec{\beta}^{(2)} (\vec{\beta}^{(4)} \wedge \vec{\beta}^{(1)} \wedge \vec{\beta}^{(1)}) = 0$$

and a similar calculation gives  $b_4^{(1)} = 0$ .

This essential result shows that for  $v \rightarrow c$  the vectors go to system of 3 pseudo-vectors in the sense of Weyssenhoff. The relations

$$a_\mu^{(\xi)} a_\nu^{(\xi)} = \delta_{\mu\nu} \quad \xi, \eta = 1, 2, 3, 4$$

$$a_\mu^{(\eta)} a_\mu^{(\xi)} = \delta^{\eta\xi} \quad \mu, \nu = 0, 1, 2, 3$$

valid for  $v \neq c$  become for  $v \rightarrow c^{(12)}$ :

$$b_i^{(r)} b_j^{(r)} = \delta_{ij} \quad r, s = 1, 2, 4$$

$$b_i^{(r)} b_i^{(s)} = \delta^{rs} \quad i, j = 1, 2, 3$$

and the system  $a_\mu^{(\xi)}$  tends towards the pseudo-vector system:

$$\begin{aligned} a_\mu^{(4)} &\rightarrow b_\mu^{(4)} = (\vec{\beta}^{(4)}, 1) \\ a_\mu^{(3)} &\rightarrow \lambda b_\mu^{(4)} \\ a_\mu^{(1)} &\rightarrow b_\mu^{(1)} = (\vec{\beta}^{(1)}, 0) \\ a_\mu^{(2)} &\rightarrow b_\mu^{(2)} = (\vec{\beta}^{(2)}, 0). \end{aligned} \tag{19}$$

The next step before we determine the limit of  $L$  is to replace the fluid density  $\varrho$  which is equal to the ordinary density in the local rest frame of the fluid at a given point by a new quantity for the velocity of light. The new quantity must evidently also satisfy the limiting form of the conservation relations

$$\partial_\mu \varrho (a_\mu^{(4)}) = 0 \tag{20}$$

as

$$a_\mu^{(4)} = \frac{1}{\tau'} a_\mu^{(4)}$$

this becomes

$$\partial_\mu \left( \frac{\varrho}{\tau'} a_\mu^{(4)} \right) = 0$$

---

<sup>12</sup> These relations are similar to the equations which define a unitary orthogonal system of ordinary vectors in three dimensions; but here they apply to pseudo-vectors at the velocity of light which we can now treat as ordinary vector variables in our Lagrangian formalism.

and if  $\tau' \rightarrow 0$  we can assume that  $\varrho/\tau' \rightarrow S_0 \neq 0$  so that the limit form of (20) is just

$$\partial_\mu (S_0 b_\mu^4) = S'_0 = 0 \quad (21)$$

As  $S_0$  depends of  $t = x_4/ic$  the relation (21) must be a consequence of the equations of motion and cannot be assumed a priori as in the usual case with  $v \neq c$ . As we shall see this follows from our treatment where there will be no Lagrange supplementary condition implying the conservation of  $S_0$ .

As an example of step b. we are now in a position to pass to the limit of Weyssenhoff's Lagrangian (6). We define this limit as the sum of the limit of various terms of the initial Lagrangian and shall justify this procedure by showing that we get correctly the relations (8) which describe Weyssenhoff particles moving with the velocity of light.

Starting from (6)

$$L = \varrho m_0 c^2 + ic p a_\mu^{(4)} \partial_\mu S + ic \varrho h_0 a_\mu^{(4)} a_\lambda^{(1)} \partial_\mu a_\lambda^{(2)} + \lambda_{\mu\nu} (a_\mu^{(\xi)} a_\nu^{(\xi)} - \delta_{\mu\nu})$$

for  $v \rightarrow c$ , we have (with  $m_0 = 0$ ):

$$\begin{aligned} \varrho &\rightarrow S_0 \tau' \\ \tau' a_\mu^{(4)} &\rightarrow b_\mu^{(4)} \\ a_\mu^{(1)} &\rightarrow b_\mu^{(1)} \\ a_\mu^{(2)} &\rightarrow b_\mu^{(2)} \\ a_\mu^{(\xi)} a_\nu^{(\xi)} - \delta_{\mu\nu} &\rightarrow b_i^{(r)} b_j^{(r)} - \delta_{ij} \end{aligned} \quad (22)$$

and, as here, according to a preceding remark concerning  $S_0$  we do not need the Lagrange parameter  $\partial_\mu S$  the equation (6) becomes at the limit  $v \rightarrow c$ .

$$L = ic S_0 h_0 b_\mu^4 b_i^1 \partial_\mu b_i^2 + \lambda_{ij} (b_i^r b_j^r - \delta_{ij}). \quad (23)$$

The deduction of relations (8) from the Lagrange function (23) is very simple.

The canonical energy momentum tensor associated to  $L$  is just:

$$\begin{aligned} t_{\mu\nu} &= \frac{\partial L}{\partial (\partial_\nu b_i^r)} \partial_\mu b_i^r - \delta_{\mu\nu} L \\ &= ic h_0 S_0 b_\nu^{(4)} b_i^{(1)} \partial_\mu b_i^{(2)} \\ &= g_\mu u_\nu; \end{aligned}$$

with:

$$g_\mu = S_0 (ic h_0 b_i^{(1)} \partial_\mu b_i^{(2)}).$$

The conservation equation  $\partial_\nu t_{\mu\nu} = 0$  is then just (5)

$$g'_\mu = 0$$

Remarking now that Euler's equation with respect to the variable  $S_0$  is  $\partial L / \partial S_0 = 0$  we find

$$g_\mu u_\mu = 0$$

that is precisely (5).

The relation  $S'_0 = 0$  results immediately from a simple combination of Euler's equations, derived from the preceding Lagrangian.

Variation of (23) with respect to  $b_i^{(1)}$  gives:

$$h_0 c S_0 b_i^{(r)'} + 2\lambda_{ij} b_j^1 = 0 \quad (a)$$

Variation of (23) with respect to  $b_i^{(2)}$  gives:

$$h_0 c b_i^{(1)} \partial_\mu (S_0 b_\mu^4) + h_0 c S_0 b_i^{(1)'} - 2\lambda_{ij} b_j^{(2)} = 0 \quad (b)$$

So if we multiply (a) by  $b_i^{(2)}$ , (b) by  $b_i^{(1)}$  and add the result we find:

$$2\lambda_{ij} (b_j^1 b_i^2 - b_j^2 b_i^1) + h_0 c S_0 (b_i^{(2)} b_i^{(2)'} + b_i^{(1)} b_i^{(1)'}) + h_0 c b_i^{(1)} b_i^{(1)} \partial_\mu (S_0 b_\mu^4) = 0$$

that is:

$$\partial_\mu (S_0 b_\mu^4) = 0;$$

since the first and second term vanish because  $b_i^{(2)} b_i^{(2)'} = b_i^{(1)} b_i^{(1)'} = 0$  and  $\lambda_{ij}$  is a symmetric tensor.

The last two relations  $m_{\mu\nu} b_\nu^4 = 0$  and  $m'_{\mu\nu} = g_\mu v_\nu - g_\nu u_\mu$  will be obtained from the Belinfante-Rosenfeld tensor  $f_{\mu\nu\lambda}$ .

Indeed utilizing definition (4) we find:

$$f_{\mu\nu\lambda} = ic h_0 S_0 (b_\mu^{(1)} b_\nu^{(2)} - b_\mu^{(2)} b_\nu^{(1)}) b_\lambda^4 = m_{\mu\nu} b_\lambda^4$$

with

$$m_{\mu\nu} = ih_0 S_0 (b_\mu^{(1)} b_\nu^{(2)} - b_\mu^{(2)} b_\nu^{(1)});$$

so that relations

$$\partial_\lambda f_{\mu\nu\lambda} = t_{\mu\nu} - t_{\nu\mu}$$

give

$$m'_{\mu\nu} = g_\mu b_\nu^4 - g_\nu b_\mu^4.$$

The last condition  $m_{\mu\nu} b_\nu^4 = 0$  results immediately from the orthogonality relations  $\beta_i^r \beta_k^r = \delta_{ik}$  deduced from the variation of the  $\lambda'_{ik}$ s.

To finish this section we would like to make two remarks.

The first is that as a result of the Lorentz contraction Weyssenhoff particles moving with the velocity of light flatten into disc shaped forms in the plane orthogonal to the velocity. The spin is then either parallel or antiparallel to the velocity. Taking into account the fact that  $\beta^1 \cdot \beta^2 = 0$  one sees immediately that the Lagrangian takes the simple form

$$L = -\frac{h_0}{2} \frac{S_0}{2} \left[ b_k^{(1)} \frac{db_k^{(2)}}{dt} - b_k^{(2)} \frac{db_k^{(1)}}{dt} \right] + \lambda_{ij} (b_i^{(r)} b_j^{(r)} - \delta_{ij}).$$



If we remark that the first term in the Lagrangian  $b_\mu^{(4)} b_l^{(4)} \partial_\mu b_l^{(2)}$  is just the scalar product of the angular velocity  $\vec{\omega}$  on the four velocity  $b_\mu^{(4)}$  we see that the equations of motion imply that this term vanishes so that the particle is reduced to a flat disc which does not rotate around its axis.

### § 3.

According to our program, the last section will include the comparison of the preceding perfect fluid constituted with Weyssenhoff particles with the hydrodynamical representation of the two component spinor theory of the neutrino<sup>5 13</sup> (recently proposed by Lee and Yang). As we shall see, this comparison shows that the two are identical when we introduce a simple type of tensions between those particles. We can thus demonstrate the following theorem:

#### Theorem

A perfect continuous fluid of Weyssenhoff particles with negligible rest mass which move with the velocity of light satisfies with suitable tensions the two component neutrino equation: the two component spinor density defining all tensor densities needed to characterize the fluids behaviour. To prove this result let us recall briefly certain mathematical elements<sup>14</sup> concerning two component spinors.

The first step is to establish a representation of 2 component spinors by tensor quantities. If one starts from a right handed coordinate frame a right handed neutrino field is represented by a right handed 2 component spinor  $\varphi^d$  (in all that follows spinors are considered as  $c$  numbers). Such a spinor transforms under a proper Lorentz transformation

$$x'_\mu = a_{\mu\nu} x_\nu \quad (1)_3$$

by

$$\varphi^d \rightarrow \varphi^{d'} = \Lambda^d \varphi^d \quad (2)_3$$

where  $\Lambda^d$  is a  $2 \times 2$  matrix defined by the relation

$$(\Lambda^d)^\dagger \sigma_\mu \Lambda^d = a_{\mu\nu} \sigma_\nu \quad (3)_3$$

where

$$\sigma_\mu = \{\sigma_k, \sigma_4\} \quad (4)_3$$

<sup>13</sup> Cf. Takabayasi, *Comptes-Rendus*, **246**, 1010 (1958).

<sup>14</sup> The transformation properties of the 2 component spinor and its associated bilinear quantities were developed in: Takabayasi, *Nucl. Physics*, **7**, 237 (1958) The general mathematical techniques to represent a two component spinor by tensor quantities is included in Takabayasi, *Prog. Th. Physics*, **14**, 283 (1955) and Takabayasi and Vigier, *Prog. Th. Physics*, **18**, 573 (1957) (especially in the Appendix).

$\sigma_k$  are just the Pauli matrices and  $\sigma_4 = i\sigma_0$  is the so-called time Pauli matrix with

$$\sigma_0 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

indices  $*$  +  $T$  have here the usual signification and denote complex conjugation, hermitian conjugation and transposition.

In the case of the neutrino we know that  $\varphi$  obeys the wave equation:

$$\partial_0 \varphi^d + \sigma_k \partial_k \varphi^d = 0 \quad (5)_3$$

i. e.

$$\sigma_\mu \partial_\mu \varphi^d = 0.$$

The complex conjugate of (5) is:

$$\partial_\mu \varphi^{d+} \sigma_\mu = 0. \quad (6)_3$$

Similarly, a left-handed neutrino field  $\varphi^s$  is represented by a different 2 component spinor (left-handed spinor)  $\varphi^s$  which transforms, under the proper Lorentz transformation (1), like

$$\varphi^s \rightarrow \varphi^{s'} = \Lambda^s \varphi^s \quad (7)_3$$

where

$$\Lambda^{s+} \sigma'_\mu \Lambda^s = a_{\mu\nu} \sigma'_\nu$$

with

$$\sigma'_\mu = \{ -\sigma_k, \sigma_4 \} = -\sigma_\mu^+$$

$\Lambda^s$  is related with  $\Lambda^d$  by:

$$\Lambda^s = (\Lambda^{d+})^{-1} \quad (8)_3$$

The wave equation satisfied by  $\varphi^s$  is:

$$\partial_0 \varphi^s - \sigma_k \partial_k \varphi^s = 0 \quad (9)_3$$

i. e.,

$$\sigma'_\mu \partial_\mu \varphi^s = 0. \quad (10)_3$$

If we consider a transformation

$$\varphi^d \rightarrow \varphi^{d\Gamma} = \Gamma \varphi^{d*} \quad (11)_3$$

where  $\Gamma$  is a 2-by-2 matrix defined by

$$\Gamma^T = -\Gamma, \quad \Gamma^+ \Gamma = 1; \quad \sigma_k^T = -\Gamma^+ \sigma_k \Gamma \quad (12)_3$$

(note that  $(\varphi^{d\Gamma})^+ = \varphi^{dT} \Gamma^+$ )

then we can show that  $\varphi^{d\Gamma}$  is a left-handed spinor. So we call the transformation (11) a chirality-conjugation.

Now, the only possible non-vanishing bilinear covariants formed with  $\varphi^d$  are the following (in so far as we do not use derivatives):

$$S_\mu^d = \varphi^{d+} \sigma_\mu \varphi^d \quad (13)_3$$

and

$$\xi_k = (\varphi^{dT})^+ \sigma_k \varphi^d = \varphi^{dT} \Gamma^+ \sigma_k \varphi^d \quad (14)_3$$

$S_\mu^d$  is a real 4-vector, while  $\xi_k$  describe 3 independent components of a self-dual tensor. In other words, writing real and imaginary parts of  $\xi_k$  as:

$$\begin{aligned} \lambda_k^{(1)} &= \frac{1}{2} (\xi_k + \xi_k^*) \\ \lambda_k^{(2)} &= \frac{1}{2i} (\xi_k - \xi_k^*) \end{aligned} \quad (15)_3$$

we see that  $\lambda_k^{(1)}$  and  $\lambda_k^{(2)}$  constitute the space and time components of a real anti-symmetric tensor  $\xi_{\mu\nu}$ ; i. e.,

$$\begin{aligned} \lambda_k^{(1)} &= \xi_{ij} \\ i \lambda_k^{(2)} &= \xi_{k4} \quad (ijk) \sim (1, 2, 3) \end{aligned} \quad (16)_3$$

Note that each of  $S_k^d$ ,  $\lambda_k^{(1)}$  and  $\lambda_k^{(2)}$  transforms as a 3-dimensional vector for pure space rotation.

We can now prove that  $S_\mu^d$  and  $\xi_k$  satisfy the following identical relations:

$$S_\mu^d S_\mu^d = 0 \quad (17)_3$$

$$\xi_k \xi_k = 0 \quad (18)_3$$

$$\xi_k S_k^d = 0. \quad (19)_3$$

It can immediately be shown<sup>15</sup> that the spinor  $\varphi^d$  is equivalently represented by the set of quantities

$$\{S_\mu^d, \xi_k\}$$

restricted by the conditions (17) — (19). Relations (17) — (19) are proved by using the formula concerning the components of Pauli matrices:

$$(\sigma_k)_{\alpha\beta} (\sigma_k)_{\alpha'\beta'} = 2\delta_{\alpha\beta'} \delta_{\alpha'\beta} - S_{\alpha\beta} S_{\alpha'\beta'}$$

(see ref. (4)), and also the properties of  $\Gamma$  matrices (12).

In terms of  $\lambda_k^{(1)}$  and  $\lambda_k^{(2)}$ , in place of  $\xi_k$ , equations (18) and (19) mean that  $\lambda_k^{(1)}$ ,  $\lambda_k^{(2)}$  and  $S_k^d$  are mutually orthogonal. Relation (17) can be rewritten as

$$(S_k^d)^2 = (S_0^d)^2 \quad (S_0^d = S_4^d/i \geq 0)$$

<sup>15</sup> See reference (14).

Furthermore, we can prove that:

$$(\lambda_k^{(1)})^2 = (\lambda_k^{(2)})^2 = (S_0^d)^2$$

with

$$\begin{vmatrix} \lambda_1^{(1)} & \lambda_2^{(1)} & \lambda_3^{(1)} \\ \lambda_1^{(2)} & \lambda_2^{(2)} & \lambda_3^{(2)} \\ S_1^d & S_2^d & S_3^d \end{vmatrix} = (S_0^d)^3 \quad (20)_3$$

If we therefore introduce unit vectors  $b_k^{(r)}$  by

$$b_k^{(r)} = \lambda_k^{(r)} / S_0^d \quad (r = 1, 2, 3) \quad (21)_3$$

$$(\lambda_k^3 = S_k^d)$$

$b_k^{(r)}$  ( $r = 1, 2, 3$ ) span a 3-dimensional right-handed orthogonal axes; thus:

$$b_k^r b_k^s = \delta_{rs} \quad b_i^r b_k^r = \delta_{ik}. \quad (22)_3$$

This completes the first step of our demonstration: the original spinor  $\varphi^d$  is now equivalently represented by the set of variables:

$$\{\lambda_k^{(r)}\} \quad (r = 1, 2, 3) \quad (23)_3$$

i. e., by

$$\{S_0^d, b_k^{(r)}\} \quad (24)_3$$

and it is now clear that any expression of  $\varphi^d$  must be representable explicitly in terms of (24). For instance bilinear quantities including 1-st order derivatives are represented as follows:

$$\varphi^{d+} \partial_\mu \varphi^d - \partial_\mu \varphi^{d+} \varphi^d = i S_0^d b_k^1 \partial_\mu b_k^2 \quad (26)_3$$

and:

$$\varphi^{d+} \sigma_k \partial_\mu \varphi^d - \partial_\mu \varphi^{d+} \sigma_k \varphi^d = -\frac{i}{2} S_0^d e_{klm} b_l^r \partial_\mu b_m^r. \quad (27)_3$$

The second step is to show how the equation of motion (5)<sub>3</sub> is representable in terms of our variables (24)<sub>3</sub>. First, we multiply (5)<sub>3</sub> by  $\varphi^{d+}$  from the left and multiply (6)<sub>3</sub> by  $\varphi^d$  from the right, then add or subtract the resulting equations, then we obtain:

$$\partial_0 (\varphi^{d+} \varphi^d) + \partial_k (\varphi^{d+} \sigma_k \varphi^d) = 0 \quad (30)_3$$

and

$$(\varphi^{d+} \partial_0 \varphi^d - \partial_0 \varphi^{d+} \varphi^d) + (\varphi^{d+} \sigma_k \partial_k \varphi^d - \partial_k \varphi^{d+} \sigma_k \varphi^d) = 0 \quad (31)_3$$

Equation (30) is nothing but

$$\partial_\mu S_\mu^d = 0$$

i. e.,

$$\partial_0 S_0^d + \partial_k (S_0^d b_k^3) = 0. \quad (32)_3$$



On the other hand, equation (31) is expressed by means of the reduction formulae (26) and (27), as

$$b_k^{(1)} \partial_0 b_k^{(2)} + \frac{1}{2} \varepsilon_{klm} b_k^{(r)} \partial_l b_m^{(r)} = 0 \quad (33)_3$$

We then proceed in the following way: first we multiply (5) by  $\sigma_i$  to obtain

$$\sigma_i \partial_0 \varphi^d + \partial_i \varphi^d + i (\sigma_k \partial_j \varphi^d - \sigma_j \partial_k \varphi^d) = 0 \quad (34)_3$$

Then we multiply (34) by  $\varphi^{d+}$  from the left, obtaining

$$\varphi^{d+} \sigma_i \partial_0 \varphi^d + \varphi^{d+} \partial_i \varphi^d + i (\varphi^{d+} \sigma_k \partial_j \varphi^d - \varphi^{d+} \sigma_j \partial_k \varphi^d) = 0 \quad (34')_3$$

then add or subtract (34') with its complex conjugate. The results are:

$$\partial_0 (\varphi^{d+} \sigma_i \varphi^d) + \partial_i (\varphi^{d+} \varphi^d) + i \{ (\varphi^{d+} \sigma_k \partial_j \varphi^d - \partial_j \varphi^{d+} \sigma_k \varphi^d) - [i, j] \} = 0 \quad (35)_3$$

and

$$(\varphi^{d+} \sigma_i \partial_0 \varphi^d - \partial_0 \varphi^{d+} \sigma_i \varphi^d) + (\varphi^{d+} \partial_i \varphi^d - \partial_i \varphi^{d+} \varphi^d) + i \{ \partial_j (\varphi^{d+} \sigma_k \varphi^d) - (j, k) \} = 0 \quad (36)_3$$

where the symbol  $(j, k)$  denotes the preceding term after permutation of the indices. By means of the reduction formulae (26)<sub>3</sub>, (27)<sub>3</sub>, these are re-written as

$$\partial_i S_o^d + \partial_o (S_o^d b_i^3) + S_o^d b_i^{(r)} \partial_l b_l^{(r)} = 0 \quad (37)_3$$

and

$$b_k^{(1)} \partial_i b_k^{(2)} - \frac{1}{2} \varepsilon_{ijk} b_j^{(r)} \partial_0 b_k^{(r)} + \frac{1}{S_o^d} \varepsilon_{ijk} \partial_j (S_o^d b_k^3) = 0 \quad (38)_3$$

The 6 real equations (37)<sub>3</sub> and (38)<sub>3</sub> are not all independent of (32)<sub>3</sub> and (33)<sub>3</sub>. The relations, which are contained in (37)<sub>3</sub> and (38)<sub>3</sub> which are independent of (32)<sub>3</sub> and (33), are only the following:

$$\partial_k (S_o^d b_k^3) = S_o^d b_k^3 \partial_0 b_k^2 \quad (39)_3$$

and

$$\partial_k (S_o^d b_k^1) = S_o^d b_k^3 \partial_0 b_k^{(1)}. \quad (40)_3$$

For instance, relation (37)<sub>3</sub> results from (39)<sub>3</sub> and (40)<sub>3</sub>, by the procedure

$$(39)_3 \times b_i^{(2)} + (40)_3 \times b_i^{(1)}.$$

In this way we have obtained 4 independent real equations:

$$\{ (32)_3, (33)_3, (39)_3, (40)_3 \} \quad (41)$$

which are equivalent to the original spinor equation (5)<sub>3</sub> (which also contains 4 real equations).

The last part of our demonstration is just to remark that our equations of motion (41)<sub>3</sub> (together with the constraints (22)<sub>3</sub>) result from the following Lagrangian density:

$$L = -\frac{\hbar c}{2} S_0^d (b_k^1 \partial_0 b_k^2 + \frac{1}{2} \varepsilon_{klm} b_k^{(r)} \partial_l b_m^{(r)}) + \lambda_{rs} (b_k^r b_k^s - \delta_{rs}) \quad (42)_3$$

From this  $L$ , we can derive the energy-momentum tensor and intrinsic angular momentum tensor of the field by the normal Belinfante-Rosenfeld procedure.

In the spinor formalism, the Lagrangian is:

$$L = -\frac{\hbar c}{2i} (\varphi^{d+} \sigma_\mu \partial_\mu \varphi^d - \partial_\mu \varphi^{d+} \sigma_\mu \varphi^d). \quad (43)_3$$

Using the reduction formulas (26)<sub>3</sub> and (27)<sub>3</sub>, (43)<sub>3</sub> is rewritten, then we get just the first term in the right-hand side of (42). Adding  $\partial_{rs} (b_k^r b_k^s - \delta_{rs})$ , we could thus at once reach the form (42)<sub>3</sub>. From this form the equations of motion (41)<sub>3</sub> can be immediately derived by variation.

The same procedure can be applied, of course, to the  $\varphi^g$  field<sup>16</sup>.

The physical interpretation of the Lagrangian (42)<sub>3</sub> is clear if we take into account the vector identity:

$$b_l^1 b_k^3 \partial_k b_l^2 + \varepsilon_{klm} b_k^3 \partial_l b_m^3 = \frac{1}{2} \varepsilon_{klm} b_k^r \partial_l b_m^r$$

which results immediately from the orthogonality conditions on the  $b_l^r$ . This relation implies that if we denote by  $L_W$  and  $L_V$  the Lagrangians (10-2) and (42-3), we have:

$$\begin{aligned} L_V &= L_W + \hbar_0 S_0^d \varepsilon_{klm} b_k^3 \partial_l b_m^3 \\ &= L_W + \Theta_{kk} \end{aligned}$$

If we denote by  $\Theta_{\mu\nu}$  the tensor  $\Theta_{\mu\nu} = \hbar_0 S_0^d \varepsilon_{k\mu l} b_k^3 \partial_r b_l^3$  that is the contribution of the  $\Theta_{kk}$  term to the canonical energy momentum tensor.

We see immediately that such a term can be interpreted as a tension term binding together the Weyssenhoff droplets (moving with  $v = c$ ), constituting the neutrino fluid. Indeed  $\Theta_{\mu\nu}$  satisfies the well-known property of ordinary tensions namely

$$\Theta_{\mu\nu} b_\nu^3 = 0$$

The physical meaning of these tensions can be understood if we remark that the divergence  $\partial_\lambda$  of the term

$$f_{\mu\nu\lambda} = \mathfrak{F}_{\mu\nu}^{rs} \frac{\partial L}{\partial (\partial_\lambda q^r)} q^s$$

(namely the Belinfante-Rosenfeld angular momentum density) is zero.

<sup>16</sup> We want to remark here that it is not at all astonishing to find that our particles are described by a two component spinor with a definite chirality. As we have seen only two possibilities arise for the velocity of light: the spin is either parallel or antiparallel to the velocity corresponding to opposite chiralities. This was also pointed out by Wigner, *Rev. Mod. Phys.*, (1957).

Calling  $f_{\mu\nu\lambda}$  the term corresponding to  $L_W$  we have then:

$$\frac{1}{2} S_0 m_{\mu\nu} = \partial_\lambda f_{\mu\nu\lambda} = \frac{1}{2} S_0 \varepsilon_{\mu\nu\alpha\beta} \partial_\alpha b_\beta^3 = \frac{1}{2} (t_{\mu\nu} - t_{\nu\mu}) \quad (44)_3$$

which is a known consequence of the neutrino equation.

Physically this means that the tension angular momentum is zero so that the orbital angular momentum  $(x_\nu t_{\mu\lambda} - x_\mu t_{\nu\lambda})$  is just equal to the variation of the particles' angular momentum. Noting that  $t_{\mu\nu} = g_\mu b_\nu^3 + \Theta_{\mu\nu}$  this can also be written:

$$\dot{m}_{\mu\nu} = g_\mu b_\nu^3 - g_\nu b_\mu^3 + \frac{1}{2} (\Theta_{\mu\nu} - \Theta_{\nu\mu})$$

which means that the variation of the total angular momentum (orbital plus spin) is just equal to the torque exerted on any given droplet by the tensions of the neighbouring fluid. We do not propose to discuss here any specific physical model which would lead to such an interaction but remark, however, that it is certainly one of the simplest possible types. Any other type resulting from a general  $\Theta_{\mu\nu}$  (function of the  $\partial_l b_l^k$ ) would in general contribute to the  $f_{\mu\nu\lambda}$  and  $\partial_\nu f_{\mu\nu\lambda}$  introducing supplementary angular momentum.

As we said before, this result can be interpreted in the following way: Consider a continuous distribution of a two component spinor satisfying the neutrino's equation  $(5)_3$ . With the help of this spinor you can determine variables by the relations  $(13)_3$  to  $(15)_3$  which satisfy  $(42)_3$  and therefore characterize completely a continuous fluid made of Weyssenhoff particles with negligible rest mass moving with the velocity of light. The lines of flow tangent to  $S_\mu^d$  are followed by the center of matter density of the corresponding droplet and the three frame  $b_k^*$  which varies along that path determines completely the evolution of all physical properties (angular momentum, etc.), which characterize Weyssenhoff's motion for such velocities.

In other words, in this last section we have used a new set of parameters  $(\varphi^d)$  instead of the E. K. variables to describe the droplet's behaviour. A similar idea had already been proposed by two of us (T. T. and J.-P. V.) to describe the motion of Weyssenhoff's particles at ordinary velocities<sup>17</sup>. Only in that case one uses 4 component normalized Dirac spinors  $\psi$  and Dirac's matrices  $\gamma_\mu$ . The correspondence with the E. K. variables  $\alpha_\mu^\xi$  is given by  $\alpha_\mu^4 = \psi^\dagger \gamma_\mu \psi$ ;  $\alpha_\mu^3 = \psi^\dagger \gamma_\mu \gamma_5 \psi$  and  $\alpha_\mu^1 + i\alpha_\mu^2 = \tilde{\psi}^\dagger \gamma_\mu \psi$ . This has also been proposed by Gürsey<sup>18</sup>.

### Conclusion

As we propose to discuss in detail in another paper some of the physical consequences of the preceding results we will limit here the discussion to a few remarks.

As we said before the first two solutions give a general method to treat the behaviour of any continuous energy-momentum and current distribution enclosed

<sup>17</sup> T. Takabayasi (unpublished). Unal and J. P. Vigiér. *Comptes-Rendus*. **245**, 1787, 1891 (1957).

<sup>18</sup> Gürsey. *Nuovo Cimento* **5**, 784 (1957).

within a time like tube by using E. K. variables. This can be applied to many physical problems and an attempt to utilize this in the case of the beams of high energy accelerators is under progress at the Institute Henri Poincaré.

The second remark is that we have obtained in sections 2 and 3 a concrete completely clear relativistic model of the hydrodynamical representation of the neutrino equation. It includes a simple "quantum coupling" corresponding to "quantum potential" terms in the hydrodynamical representations of the other quantum equations. It shows that the neutrino equation can be interpreted 1) as governing the evolution of a probability distribution of neutrinos (with density  $S_0^d$ ) as in the usual interpretation of quantum mechanics or 2) as describing a real perfect continuous fluid of Weysenhoff with zero rest mass moving with the velocity of light connected by the tensions  $\Theta_{\mu\nu}$  3) as giving a real physical model of the behaviour of the real physical wave  $u$  associated with the neutrino in the causal interpretation of quantum mechanics proposed by de Broglie, Bohm and one of us (J.-P. Vigiér)<sup>19</sup>.

The third and last remark is that such an hydrodynamical representation of the neutrino equation paves the way to many interesting developments. For example in a subsequent paper we shall demonstrate that a mixture of two such perfect fluids with a spin-spin interaction leads to hydrodynamical equations which when expressed in spinor variables correspond exactly to the non-linear equation recently proposed by Heisenberg and Iwanenko<sup>20</sup>.

We wish to express our gratitude to Professors L. de Broglie, D. Bohm and to Dr. F. Halbwachs for the interest shown in this work and for various valuable suggestions. Professor Bohm in particular has greatly contributed to the clarification of our model.

### Appendix

To demonstrate that at the velocity of light the set of E. K. variables  $a_\mu^\xi$  transform into the three orthogonal pseudo-vectors  $b_k^r$ , we can proceed in the following way: we have the following relations:

$$a_\mu^{(4)} = \frac{u_\mu}{i c}, \quad a_\mu^{(3)} = \frac{i}{2ch_0} \varepsilon_{\mu\nu\alpha\beta} a_\nu^{(4)} s^{\alpha\beta}, \quad a_\mu^{(1)} = \varepsilon_{\mu\nu\alpha\beta} a_\nu^{(2)} a_{(\alpha}^{(3)} a_{\beta)}^{(4)} \quad (1)$$

and

$$b'^{(4)} a_\mu^\xi a_\nu^\xi = \delta_{\mu\nu} a_\mu^\xi a_\mu^\eta = \delta^{\xi\eta} (\mu, \nu, \xi, \eta \sim 1, 2, 3, 4) \quad (2)$$

we defined the parameter  $b'$

$$b' = \frac{db}{dt} = \sqrt{1 - \frac{v^2}{c^2}} \quad (3)$$

<sup>19</sup> See for example: De Broglie „*Une Interpretation Causale et non-linéaire de la Mécanique*“. David Bohm, *Phys. Rev.* David Bohm and J.-P. Vigiér, *Phys. Rev.* The theory is also summarized in Halbwachs, see ref. 3.

<sup>20</sup> That is  $\gamma_\mu \partial_\mu \Psi - \chi \{ \Psi^+ \Psi - (\Psi^+ \gamma_5 \Psi) \gamma_5 \} \Psi = 0$ .



if we take:

$$w_\mu = b' \mu_\mu, \quad a_\mu^{(3)} \text{ and } a_\mu^{(4)} \text{ become } b' a_\mu^{(3)}, b' a_\mu^{(4)}$$

so:

$$(b' a_\mu^{(3)}) (b' a_\mu^{(3)}) = (b' a_\mu^{(4)}) (b' a_\mu^{(4)}) = b'^2 \quad (4)$$

now if we define:

$$\beta_\mu^{(3)} = \lim_{b' \rightarrow 0} b' a_\mu^{(3)}, \quad \beta_\mu^{(4)} = \lim_{b' \rightarrow 0} b' a_\mu^{(4)} \quad (5)$$

and we have:

$$\beta_\mu^{(3)} \beta_\mu^{(3)} = \beta_\mu^{(4)} \beta_\mu^{(4)} = 0 \quad (6)$$

$$\beta_\mu^{(3)} \beta_\mu^{(4)} = 0 \quad (7)$$

it results immediately from Schwarz inequality that:

$$\beta_\mu^{(3)} = i \lambda \beta_\mu^{(4)} \quad (8)$$

where  $\lambda$  is a real scalar.

Let us choose:

$$\beta_4^{(4)} = 1 \quad b_h^{(4)} = i \beta_h^{(4)} \quad (h \sim 1, 2, 3) \quad (9)$$

$b_h^{(4)}$  is like a two dimensional unitary vector and

$$b_h^{(4)} b_h^{(4)} = 1 \quad (10)$$

Let us prove that  $\lambda = \pm 1$ . For this, let us start with the relation:

$$a_\mu^{(2)} a_\nu^{(3)} - a_\mu^{(3)} a_\nu^{(2)} = \varepsilon_{\mu\nu\alpha\beta} a_\alpha^{(4)} a_\beta^{(1)}$$

which multiplied by  $b'$  and going to the limit (taking into account the relation (8))

$$i \lambda (a_\mu^{(2)} \beta_\nu^{(4)} - a_\nu^{(2)} \beta_\mu^{(4)}) = \varepsilon_{\mu\nu\alpha\beta} \beta_\alpha^{(4)} a_\beta^{(1)}$$

the space components taken out of this expression are:

$$i \lambda (a_0^{(2)} \beta_j^{(4)} - a_j^{(2)} \beta_0^{(4)}) = \varepsilon_{ijk4} \beta_k^{(4)} a_4^{(1)}$$

and, as we have:  $a_4^{(1)} = i a_0^{(1)}$   $\beta_j^{(4)} = -i b_j^{(4)}$   $\beta_4^{(4)} = 1$

$$\lambda (\vec{a}^{(2)} \wedge \vec{b}^{(4)}) = a_0^{(1)} \vec{b}^{(4)} - \vec{a}^{(1)} \quad (11)$$

where the symbol  $\rightarrow$  denotes a three dimensional vector.

From (11), we have:

$$\lambda^2 (\vec{a}^{(2)} \wedge \vec{b}^{(4)}) (\vec{a}^{(2)} \wedge \vec{b}^{(4)}) = (a_0^{(1)} \vec{b}^{(4)} - \vec{a}^{(1)}) (a_0^{(1)} \vec{b}^{(4)} - \vec{a}^{(1)})$$

$$\lambda^2 [(\vec{a}^{(2)} \cdot \vec{a}^{(2)}) (\vec{b}^{(4)} \cdot \vec{b}^{(4)}) - (\vec{a}^{(2)} \cdot \vec{b}^{(4)})^2] = a_0^{(1)} a_0^{(1)} \vec{b}^{(4)} \cdot \vec{b}^{(4)} + \vec{a}^{(1)} \cdot \vec{a}^{(1)} - 2 a_0^{(1)} \vec{a}^{(1)} \cdot \vec{b}^{(4)}$$



taking into account relation (2):

$$\begin{aligned}\vec{a}^{(1)} \cdot \vec{a}^{(1)} &= 1 + a_0^{(1)} a_0^{(1)} & \vec{a}^{(2)} \cdot \vec{a}^{(2)} &= 1 + a_0^{(2)} a_0^{(2)} \\ \vec{a}^{(1)} \cdot \vec{b}^{(4)} &= a_0^{(1)} & \vec{a}^{(2)} \cdot \vec{b}^{(4)} &= a_0^{(2)}\end{aligned}$$

and relation (10):

it comes for the preceding expression:  $\lambda^2 = 1$

and finally:

$$\beta_\mu^{(3)} = \pm i \beta_\mu^{(4)}$$

Now to obtain the limits for  $a_\mu^{(1)}$  and  $a_\mu^{(1)}$  let us suppose  $b'$  sufficiently weak to enable us to write:

$$b' a_\mu^{(3)} = i \beta_\mu^{(4)} + b'^2 \delta_\mu^{(3)} + O_1(b'^2) \quad (12)$$

$$b' a_\mu^{(4)} = \beta_\mu^{(4)} + i b'^2 \delta_\mu^{(4)} + O_2(b'^2) \quad (13)$$

where  $\delta_\mu^{(3)}$  and  $\delta_\mu^{(4)}$  are space-like vectors,  $O_1(b'^2)$  and  $O_2(b'^2)$  are negligible quantities.

For  $b' \neq 0$ ,  $b' a_\mu^{(3)}$ , and  $b' a_\mu^{(4)}$  are not isotropic vectors and their norm must be positive; of course, they are always orthogonal so we have

$$i \beta_\mu^{(4)} \delta_\mu^{(3)} > 0 \quad (14)$$

$$i \beta_\mu^{(4)} \delta_\mu^{(4)} > 0 \quad (15)$$

$$i \beta_\mu^{(4)} (\delta_\mu^{(3)} - \delta_\mu^{(4)}) = 0 \quad (16)$$

Moreover  $\delta_0^{(4)} = 0$  as  $\beta_4^{(4)} = 1$  and:

$$b' a_\mu^{(4)} = \frac{b'}{\sqrt{1 - \frac{v^2}{c^2}}} = 1$$

we conclude:  $b'^2 \delta_0^{(4)} = 0$  or  $\delta_0^{(4)} = 0$

let us apply (12) and (13) to the relation:

$$b' a_\mu^{(3)} = \varepsilon_{\mu\nu\alpha\beta} a_\alpha^{(1)} a_\beta^{(2)} (b' a_\nu^{(4)})$$

we obtain:

$$i \beta_\mu^{(4)} + b'^2 \delta_\mu^{(3)} = \varepsilon_{\mu\nu\alpha\beta} a_\alpha^{(1)} a_\beta^{(2)} (\beta_\nu^{(4)} + i b'^2 \delta_\nu^{(4)})$$

or:

$$i \beta_\mu^{(4)} = \varepsilon_{\mu\nu\alpha\beta} a_\alpha^{(1)} a_\beta^{(2)} \beta_\nu^{(4)} \quad (17)$$

$$\delta_\mu^{(3)} = i \varepsilon_{\mu\nu\alpha\beta} a_\alpha^{(1)} a_\beta^{(2)} \delta_\nu^{(4)} \quad (18)$$

The relation (18) gives:

$$-\delta_0^{(3)} = \vec{\delta}^{(4)} \cdot (\vec{a}^{(1)} \wedge \vec{a}^{(2)}) \quad (19)$$

$$\delta_i^{(3)} = -\delta_0^{(4)} (\vec{a}^{(1)} \wedge \vec{a}^{(2)})_i - a_0^{(2)} (\vec{\delta}^{(4)} \wedge \vec{a}^{(1)})_i - a_0^{(1)} (\vec{a}^{(2)} \wedge \vec{\delta}^{(4)})_i \quad (20)$$

Now, let us start with the relation:

$$b' a_{\mu}^{(4)} = \varepsilon_{\mu\nu\alpha\beta} a_{\nu}^{(1)} a_{\alpha}^{(2)} a_{\beta}^{(3)}$$

The same calculation brings to:

$$-\delta_0^{(4)} = \vec{\delta}^{(3)} \cdot (\vec{a}^{(1)} \wedge \vec{a}^{(2)}) \quad (21)$$

$$\delta_i^{(4)} = -\delta_0^{(3)} (\vec{a}^{(1)} \wedge \vec{a}^{(2)})_i - a_0^{(2)} (\vec{\delta}^{(3)} \wedge \vec{a}^{(1)})_i - a_0^{(1)} (\vec{a}^{(2)} \wedge \vec{\delta}^{(3)})_i \quad (22)$$

As  $\delta_0^{(4)} = 0$  the equation (21) has two solutions:

$$\vec{\delta}^{(3)} = \lambda \vec{a}^{(1)} + \mu \vec{a}^{(2)} \quad (23)$$

$$\delta^{(3)} = 0 \quad (24)$$

Let us consider the first solution. Let us multiply (20), by  $\vec{a}^{(1)}$  and by  $\vec{a}^{(2)}$  taking into account relation (19); we have:

$$\vec{\delta}^{(3)} \cdot \vec{a}^{(1)} = a_0^{(1)} \delta_0^{(3)} \quad \vec{\delta}^{(3)} \cdot \vec{a}^{(2)} = a_0^{(2)} \delta_0^{(3)} \quad (25)$$

Because the orthogonality conditions, when we put (23) into (25) we obtain the system:

$$\begin{aligned} \lambda + \lambda (a_0^{(1)})^2 + \mu a_0^{(1)} a_0^{(2)} &= a_0^{(1)} \delta_0^{(3)} \\ \lambda a_0^{(1)} a_0^{(2)} + \mu + \mu a_0^{(2)} a_0^{(2)} &= a_0^{(2)} \delta_0^{(3)} \end{aligned} \quad (26)$$

The solution is:

$$\lambda = a_0^{(1)}, \quad \mu = a_0^{(2)}, \quad \delta_0^{(3)} = 1 + (a_0^{(1)})^2 + (a_0^{(2)})^2 \quad (27)$$

Now, with  $\vec{\delta}^{(3)}$  it is possible to calculate  $\vec{\delta}^{(4)}$ . It's sufficient to multiply successively (22) by  $a^{(1)}$  and  $a^{(2)}$ , this gives:

$$\vec{\delta}^{(4)} \cdot \vec{a}^{(1)} = \vec{\delta}^{(4)} \cdot \vec{a}^{(2)} = 0$$

or

$$\vec{\delta}^{(4)} = \nu (\vec{a}^{(1)} \wedge \vec{a}^{(2)}) \quad (28)$$

If we bring (28) into (19):

$$\begin{aligned} -\delta_0^{(3)} &= \nu (\vec{a}^{(1)} \wedge \vec{a}^{(2)}) \cdot (\vec{a}^{(1)} \wedge \vec{a}^{(2)}) = \nu [(\vec{a}^{(1)} \cdot \vec{a}^{(1)}) (\vec{a}^{(2)} \cdot \vec{a}^{(2)}) - (\vec{a}^{(1)} \cdot \vec{a}^{(2)})^2] = \\ &= \nu [1 + (a_0^{(1)})^2 + (a_0^{(2)})^2] = \nu \delta_0^{(3)} \end{aligned}$$

This implies:  $\nu_0 = -1$

and:

$$\vec{\delta}^{(4)} = -(\vec{a}^{(1)} \wedge \vec{a}^{(2)}) \quad (29)$$

But the relation (14) writes:

$$\vec{b}^4 \cdot \vec{\delta}^{(4)} > 0 \quad (30)$$

and the relation (17) gives:

$$\vec{b}^4 \cdot (\vec{a}^{(1)} \wedge \vec{a}^{(2)}) = 1 \quad (31)$$

We see that (29), (30), and (31) are not compatible.

Now we have the second solution  $\vec{\delta}^{(3)} = 0$

From (22):

$$\delta_i^{(4)} = -\delta_0^{(3)} (\vec{a}^{(1)} \wedge \vec{a}^{(2)})_i \quad (32)$$

which implies (16), moreover (14), (15), (31) are verified if  $\delta_0^{(3)} < 0$ . But bringing (12) and (13) into the expression:

$$(a_\mu^{(1)} a_\nu^{(2)} - a_\mu^{(2)} a_\nu^{(1)}) b'^2 = \varepsilon_{\mu\nu\alpha\beta} (b' a_\alpha^{(3)}) (b' a_\beta^{(4)})$$

a direct calculation gives:

$$\vec{a}^{(1)} \wedge \vec{a}^{(2)} = \vec{\delta}^{(3)} + \vec{\delta}^{(4)} - (\delta_0^{(3)} + \delta_0^{(4)}) \vec{b}^{(4)} = -\delta_0^{(3)} (\vec{a}^{(1)} \wedge \vec{a}^{(2)} + \vec{b}^{(4)})$$

let us multiply this result by  $\vec{b}^{(4)}$ , taking into account the relation (31) and  $\vec{b}^{(4)} \cdot \vec{b}^{(4)} = 1$  we have:

$$s = -2\delta_0^{(3)} \text{ or } \delta_0^{(3)} = -\frac{1}{2}$$

that is what we intend. Besides putting (32) into (19), we find:

$$(\vec{a}^{(1)} \wedge \vec{a}^{(2)}) \cdot (\vec{a}^{(1)} \wedge \vec{a}^{(2)}) = 1$$

which implies

$$(a_0^{(1)})^2 + (a_0^{(2)})^2 = 0$$

or

$$a_0^{(1)} = a_0^{(2)} = 0$$

this is the resulte which we wanted to prove.

## ERRATA

“Nuclear Charge Effect on the Free-Electron Model Energy States” S. Olszewski (*Acta phys. Polon.* **18**, 107 (1959))

Formula (13): At the beginning of each of the three last lines of the formula: instead of the “+” sign it should be “—” sign.

Table III & IIIa, fifth column: instead of  $Z_{eff} = \frac{2}{3}$  it should be  $Z_{eff} = \frac{2}{n_c}$ ; sixth column: instead of  $Z_{eff} = \frac{1}{3}$  it should be  $Z_{eff} = \frac{1}{n_c}$ .

“On the Coulomb and Exchange Operators in the Free-Electron Model” S. Olszewski (*Acta phys. Polon.* **18**, 121 (1959))

Formula (1b) should have the form:

$$\mathcal{K}_i \varphi(\mathbf{r}) = e^2 \left( \int \frac{\varphi_i(\mathbf{r}') \varphi(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\tau' \right) \varphi_i(\mathbf{r}) \quad (1b)$$

Formula ( $\alpha$ ), footnote 2, should have the form:

$$C = \lim_{R \rightarrow 0} \frac{e^2}{(\pi R^2)^2} \int \cos cz' \cos az \frac{1}{|\mathbf{r} - \mathbf{r}'|} d\tau' d\tau = \quad (\alpha)$$

$$= e^2 \left[ \frac{1}{2n} \{Si(m+n) + Si(n-m)\} + \frac{1}{2m} \{-Si(n+m) + Si(n-m)\} \right]$$

Formula (not numbered), coming after formula (11), should be

$$\int \cos az \mathcal{C}'_0 dz = \frac{e^2}{L} Si(aL) \frac{2}{a}$$

Page 131, line 7 (from the top): instead of  $\frac{1}{2} (\mathcal{C}'_0 - \mathcal{C}'_c)$  it should be:  $\mathcal{C}'_0 - \mathcal{C}'_c$ .

Formula (25) should be:

$$H\psi_i(z) + \left\{ 2 \sum_{\substack{k=1 \\ k \neq i}}^{N/2} (-1) \frac{e^2}{L} [\log z + \log(L-z) - 2 \log L - 1 - \cos cz Ci(cz) - \right.$$

$$- \cos c(L-z) Ci[c(L-z)] - \sin cz Si(cz) - \sin c(L-z) Si[c(L-z)]] + \quad (25)$$

$$\left. + \frac{e^2}{L} (-1) \cdot (1 - W_{\frac{N}{2}}) [\log z + \log(L-z) - 2 \log L - 1] \right\} \psi(z) = E\psi_i(z)$$







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